

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-257419

(43)Date of publication of application : 19.09.2000

(51)Int.Cl.

F01N 3/24
B01D 53/86
B01D 53/94
B01J 29/22
F01N 3/08
F01N 3/10
F01N 3/20
F01N 3/36

(21)Application number : 11-055554

(22)Date of filing : 03.03.1999

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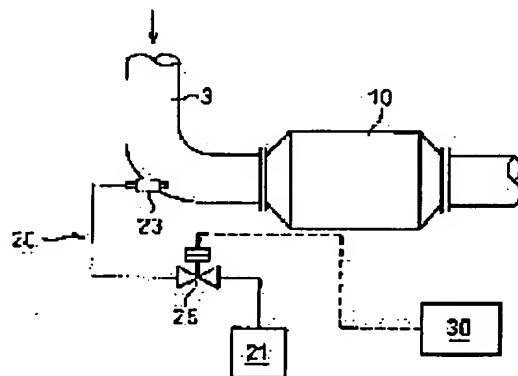
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(54) EXHAUST PURIFICATION METHOD AND DEVICE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To attain high NOX purification efficiency without adjusting exhaust to a rich air-fuel ratio by generating a low temperature oxidation reaction after supplying reductant, while retaining exhaust purification catalyst in a prescribed temperature range, and continuously producing reaction activated substance such that combustion exhaust at a specified air excess ratio is supplied.

SOLUTION: A reductant supply device 20 for supplying liquid reductant is provided upstream of exhaust purification catalyst (RAP catalyst) 10 disposed in an exhaust passage 3. The RAP catalyst is obtained by carrying oxidized catalyst components, such as Pt and Pd on the multi-porous zeolite. A combustion state in an engine 1 is adjusted, such that an excess air ratio of the combustion exhaust flowing through the exhaust passage 3 becomes 1.0 or more. The flow rate of the reductant injected from a nozzle 23 is controlled by adjusting an opening degree of a control valve 25 in a control device 30. Furthermore, by allowing the exhaust temperature and excess air ratio to be within the range where a low-temperature oxidation reaction takes place on the catalyst, the reductant is converted into a radical and reacts preferentially with NOX in the exhaust, realizing high purification efficiency.



LEGAL STATUS

[Date of request for examination] 19.07.2002

[Date of sending the examiner's decision of rejection] 06.04.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application]

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CLAIMS

[Claim(s)]

[Claim 1] The reducing agent supplied in the temperature field higher than a predetermined temperature field is burned under existence of oxygen including an oxidation catalyst component. The exhaust air purification catalyst which performs the low-temperature-oxidation reaction which oxidizes the reducing agent supplied in said predetermined temperature field, without following combustion on the bottom of existence of oxygen, and generates the labile matter continuously is arranged to a flueway. By supplying a reducing agent to an exhaust air purification catalyst, maintaining said exhaust air purification catalyst to said predetermined temperature field, produce said low-temperature-oxidation reaction of a reducing agent, generate said labile matter continuously, and an excess air factor supplies 1.0 or more combustion exhaust air to said exhaust air purification catalyst. NOX under said labile matter generated on said exhaust air purification catalyst, and exhaust air It is made to react and is NOX under exhaust air. The exhaust air purification approach which carries out reduction purification.

[Claim 2] The exhaust air purification approach according to claim 1 which makes 1.0 or more and 1.7 or less the excess air factor of the combustion exhaust air supplied to said exhaust air purification catalyst.

[Claim 3] Said exhaust air purification catalyst is the exhaust air purification approach according to claim 1 or 2 that the oxidation capacity according an oxidation catalyst component and a reduction catalyst component to an oxidation catalyst component respectively and the reduction capacity by the reduction catalyst component contain only the amount to which it becomes almost equivalent.

[Claim 4] Said exhaust air purification catalyst is the exhaust air purification approach given in any 1 term of claim 1 to claim 3 which holds the supplied reducing agent in a catalyst and generates said labile matter continuously on a catalyst by producing the low-temperature-oxidation reaction of said held reducing agent in said predetermined temperature field under oxygen existence.

[Claim 5] With possible holding the reducing agent supplied to an internal combustion engine's flueway, and making a reduction component and NOX under exhaust air react to whenever [more than predetermined activation temperature / catalyst temperature] alternatively under a hyperoxia ambient atmosphere By arranging the exhaust air purification catalyst containing an oxidation catalyst component, supplying a reducing agent to this exhaust air purification catalyst, and making more highly than the boiling point of said reduction component whenever [said exhaust air purification catalyst temperature] into a predetermined temperature field lower than said activation temperature under a hyperoxia ambient atmosphere NOX under the labile matter which was made to produce the low-temperature-oxidation reaction which oxidizes without following combustion on said reduction component, and generates the labile matter, and was generated, and engine exhaust air It is made to react and is NOX under exhaust air. The exhaust air purification approach of the internal combustion engine which does reduction purification.

[Claim 6] The exhaust air purification approach of the internal combustion engine according to claim 5 which supplies said reducing agent to said exhaust air purification catalyst before said internal combustion engine's starting.

[Claim 7] Said exhaust air purification catalyst is the exhaust air purification approach of the internal combustion engine according to claim 5 or 6 which can stick to a catalyst component front face about said labile matter which supported platinum or palladium as a catalyst component, and generated it.

[Claim 8] The exhaust air purification approach of an internal combustion engine given in any 1 term of claim 5 to claim 7 which generates said labile matter continuously on a catalyst by said low-temperature-oxidation reaction, and supplements a catalyst with the consumed labile matter by performing supply of a reducing agent continuously.

[Claim 9] The exhaust air purification approach of the internal combustion engine according to claim 5

which makes said labile matter of the amount of requests generate on a catalyst by using a liquefied hydrocarbon as said reducing agent, and changing at least one side of whenever [amount-of-supply / of the reducing agent to a catalyst /, or catalyst temperature] according to the description of a hydrocarbon.

[Claim 10] The exhaust air purification approach of the internal combustion engine according to claim 5 which the specific constituent concentration under exhaust air after passing said exhaust air purification catalyst is detected [internal combustion engine], and changes the reducing-agent conditions of supply to said exhaust air purification catalyst according to the concentration of this specific component.

[Claim 11] Furthermore, the exhaust air purification approach of the internal combustion engine according to claim 5 which arranges the possible upstream exhaust air purification catalyst of making the reducing agent supplied to the upstream of said exhaust air purification catalyst in said predetermined temperature field including the oxidation catalyst component produce a low-temperature-oxidation reaction, and was made to become small from the oxidation capacity of the exhaust air purification catalyst of the downstream about the oxidation capacity of this upstream exhaust air purification catalyst.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is NOX under Lean air-fuel ratio exhaust air with an excess air factor higher than 1 in a detail about the exhaust air purification approach. It is related with the exhaust air purification approach to purify.

[0002]

[Description of the Prior Art] An excess air factor is higher than 1, namely, it is NOX under exhaust air of a hyperoxia ambient atmosphere (Lean air-fuel ratio). As an exhaust air purification catalyst used for purification, it is NOX. The occlusion reduction catalyst and the selection reduction catalyst are known. NOX An occlusion reduction catalyst is nitrate ion NO₃ about NOX under exhaust air (NO₂, NO), when the air-fuel ratio of the exhaust gas which is what supported components, such as barium (Ba), and noble metals like platinum (Pt), and flows on support, such as an alumina, is Lean. - NOX which absorbed in the form, and was absorbed when the oxygen density of inflow exhaust gas fell The absorption/emission action of NOX to emit is performed. For example, it is NOX about exhaust air of the Lean air-fuel ratio. If an occlusion reduction catalyst is supplied, it is NOX under exhaust air. NOX It is absorbed by the occlusion reduction catalyst and is NOX. It is removed from exhaust air. Moreover, NOX Absorbed NOX The reducing agent supplied when reducing agents, such as a hydrocarbon, were supplied to the occlusion reduction catalyst is NOX. It oxidizes on an occlusion reduction catalyst and is NOX. The ambient atmosphere oxygen density of an occlusion reduction catalyst falls. Thereby, it is NOX. From an occlusion reduction catalyst, it is NOX. It is emitted and is NOX by the reducing agent under exhaust air. Reduction purification is carried out on an occlusion reduction catalyst.

[0003] moreover, a selection reduction catalyst -- for example, a zeolite -- as a catalyst component -- copper (Cu) -- the ion exchange etc. -- or the object which made platinum (Pt) support according to sinking in etc. is used. A selection reduction catalyst is NOX under existence of HC of optimum dose, CO, etc., when an exhaust air air-fuel ratio is Lean. It is NOX under exhaust air by making HC, CO, and a selection target react. It returns and is N₂. It has the function to convert. That is, in a selection reduction catalyst, if components, such as a hydrocarbon (HC), exist during the flowing exhaust air, the pore of a zeolite will be adsorbed in these HC component etc. Moreover, in metal components, such as platinum of a selection reduction catalyst, and copper, it is NOX under exhaust air under the Lean air-fuel ratio. A component adsorbs. And components, such as HC by which the zeolite was adsorbed, are NOX which encroaches on a front face in a fixed temperature requirement and by which front faces, such as platinum and copper, were adsorbed. It reacts preferentially and is NOX. Reduction purification is carried out.

[0004] As an example of the exhaust emission control device using such an exhaust air purification catalyst, there are some which were indicated by JP,4-330314,A, for example. The equipment of this official report has arranged the selection reduction catalyst which used the copper-zeolite for a Diesel engine's flueway, and has formed a means to inject the fuel as a reducing agent in the flueway of the catalyst upstream. The fuel quantity injected to a flueway according to the hydrocarbon concentration under engine exhaust air in the temperature field beyond the temperature (activation temperature) which a selection reduction catalyst activates is controlled by the equipment of this official report, and the oxygen of optimum dose is always made to be supplied to a selection reduction catalyst. Thereby, it is NOX under Lean air-fuel ratio exhaust air from a Diesel engine. Reduction purification is carried out by the hydrocarbon component of which the selection reduction catalyst was adsorbed.

[0005]

[Problem(s) to be Solved by the Invention] However, the Lean air-fuel ratio is exhausting using a selection

reduction catalyst like the equipment of the above-mentioned official report, a reducing agent is supplied to a selection reduction catalyst, and it is NOX under exhaust air. In purifying, there is a problem from which the high rate of purification of NOX is not obtained. Since platinum, copper, etc. with which this is supported by the selection reduction catalyst function as an oxidation catalyst, in a hyperoxia ambient atmosphere, a hydrocarbon component is NOX. It is because oxygen and a reaction are produced. That is, when it is [Lean air-fuel ratio] under exhaust air and a reducing agent is supplied to a selection reduction catalyst, the most burns on a catalyst and the supplied hydrocarbon (or it invaded from the selection reduction catalyst) is CO₂ as H₂ O. They are a hydrocarbon and NOX in order to form. It is hard coming to generate a reaction and is high NOX. The rate of purification cannot be obtained.

[0006] On the other hand, it is NOX. It is NOX when an occlusion reduction catalyst is used. Since emission and reduction purification are performed in reducing atmosphere (rich air-fuel ratio), the high rate of purification of NOX can be obtained as compared with a selection reduction catalyst. However, NOX An occlusion reduction catalyst to NOX It is NOX, in order to make it emit and to carry out reduction purification. It is necessary to make lower than 1.0 the excess air factor of the exhaust air which flows into an occlusion reduction catalyst (to rich air-fuel ratio). For this reason, NOX An occlusion reduction catalyst to NOX It is NOX when an engine is temporarily switched to rich air-fuel ratio operation in the gasoline engine which usually sometimes performs the Lean air-fuel ratio operation, for example when it should be made to emit, or rich air-fuel ratio operation supplies a lot of reducing agents to a flueway in a difficult Diesel engine. There was a problem for which complicated actuation of adjusting temporarily the air-fuel ratio of the exhaust air which flows into an occlusion reduction catalyst to a rich air-fuel ratio is needed.

[0007] Moreover, this invention is high NOX, without adjusting the air-fuel ratio of exhaust air to a rich air-fuel ratio in view of the problem of the conventional exhaust air purification catalyst mentioned above. It aims at offering the exhaust air purification approach that purification effectiveness can be attained.

[0008]

[Means for Solving the Problem] According to invention according to claim 1, the reducing agent supplied in the temperature field higher than a predetermined temperature field is burned under existence of oxygen including an oxidation catalyst component. The exhaust air purification catalyst which performs the low-temperature-oxidation reaction which oxidizes the reducing agent supplied in said predetermined temperature field, without following combustion on the bottom of existence of oxygen, and generates the labile matter continuously is arranged to a flueway. By supplying a reducing agent to an exhaust air purification catalyst, maintaining said exhaust air purification catalyst to said predetermined temperature field, produce said low-temperature-oxidation reaction of a reducing agent, generate said labile matter continuously, and an excess air factor supplies 1.0 or more combustion exhaust air to said exhaust air purification catalyst. NOX under said labile matter generated on said exhaust air purification catalyst, and exhaust air It is made to react and is NOX under exhaust air. The exhaust air purification approach which carries out reduction purification is offered.

[0009] That is, in invention of claim 1, the low-temperature-oxidation reaction of a reducing agent generates the labile matter continuously, and it is NOX under this labile matter and exhaust air. It is made to react and is NOX. Reduction purification is carried out. Labile matter here is radicals (free radical), such as a hydrocarbon. usually, the radical generated although HC radical occurred as an intermediate product in the oxidization process also when a hydrocarbon (HC) oxidized under a hyperoxia ambient atmosphere by the strong (activated) oxidation catalyst of oxidizing power etc. -- immediately -- oxygen -- reacting -- CO₂ etc. -- it changes. That is, if HC oxidizes on the strong oxidation catalyst of oxidizing power, combustion of a hydrocarbon will arise.

[0010] If a reducing agent is oxidized in the low-temperature field where the activity of an oxidation catalyst is low, the radical generated by oxidization of a reducing agent will not react with ***** immediately, but the condition of a radical will be maintained. Moreover, in order for the reducing agent which was late compared with the case where the activity of a catalyst is high as for the oxidation rate of a reducing agent, and was supplied not to oxidize at once but to oxidize small quantity every comparatively in this case, on a catalyst, a radical comes to occur continuously. On these specifications, the oxidation reaction (oxidation reaction by which a radical component is generated continuously) without above-mentioned combustion in the low-temperature field of a catalyst is called the low-temperature-oxidation reaction. Moreover, a low-temperature-oxidation reaction can also be said to be the oxidation reaction to which the heat of reaction generated by oxidation reaction of a reducing agent becomes lower than the calorific value of the proper which a reducing agent has. radicals, such as a hydrocarbon, -- labile -- very much -- strong -- the bottom of existence of oxygen -- also setting -- NOX etc. -- it reacts preferentially with the unstable matter chemically.

[0011] In invention of claim 1, an oxidation catalyst is used in the field of comparison-low temperature lower than activation temperature, and reducing agents, such as a hydrocarbon, are supplied to a catalyst under a hyperoxia ambient atmosphere, supplying exhaust air of the Lean air-fuel ratio to a catalyst. The radical which radicals, such as a hydrocarbon, were continuously generated on the catalyst, and was come and generated by this is NOX under exhaust air. It reacts and is NOX. Reduction purification is carried out. That is, the radical of the reducing agent produced by the low-temperature-oxidation reaction is used, and it is NOX. By returning, it is NOX under exhaust air at high effectiveness, with a hyperoxia ambient atmosphere maintained. It becomes possible to carry out reduction purification.

[0012] In addition, when a gas-like reducing agent is supplied to a catalyst, the generation rate of the radical by the low-temperature-oxidation reaction becomes excessive, while the radical generated superfluously reacts with oxygen and is consumed, whenever [catalyst temperature] goes up by the reaction, and there is a possibility of being hard that it may come to generate a low-temperature-oxidation reaction. For this reason, when using a liquid-like thing and making it a low-temperature-oxidation reaction arise through the process of the evaporation on a catalyst, as for the reducing agent supplied to a catalyst, it is desirable that a radical is continuously generated at a comparatively low rate.

[0013] According to invention according to claim 2, the exhaust air purification approach according to claim 1 which makes 1.0 or more and 1.7 or less the excess air factor of the combustion exhaust air supplied to said exhaust air purification catalyst is offered. That is, it is controlled by invention according to claim 2 by the conditions which the ambient atmosphere oxygen density of an exhaust air purification catalyst tends to generate continuously [a radical] at a low-temperature-oxidation reaction. Oxygen is needed in order for the low-temperature-oxidation reaction of a reducing agent to generate a radical. For this reason, the excess air factor of the exhaust air supplied to an exhaust air purification catalyst needs to be 1.0 or more. On the other hand, although the generation rate of a radical becomes quick as the oxygen density under exhaust air becomes high, the reducing agent supplied in this case may change to a radical for a short time, and it may become difficult to realize the condition that a radical exists continuously on a catalyst. As a result of an experiment, in order to realize the condition that continue on a catalyst and the radical of a reducing agent exists, it has become clear that 1.0 or more and 1.7 or less range has a desirable excess air factor. The reducing agent supplied by making or less [1.0 or more] into 1.7 the excess air factor of the exhaust air supplied to an exhaust air purification catalyst in this invention is made to generate a radical continuously on a catalyst, and it is NOX under exhaust air. Reduction purification is enabled continuously.

[0014] According to invention according to claim 3, the exhaust air purification approach according to claim 1 or 2 that the oxidation capacity according [said exhaust air purification catalyst] an oxidation catalyst component and a reduction catalyst component to an oxidation catalyst component respectively and the reduction capacity by the reduction catalyst component contain only the amount which becomes almost equivalent is offered. That is, in addition to the oxidation catalyst component, the exhaust air purification catalyst contains the reduction catalyst component, and he is trying for the reduction capacity of a reduction catalyst component to rival the oxidation capacity of an oxidation catalyst component mostly in invention according to claim 3. The reducing agent supplied when the oxidation capacity of a catalyst was high, as mentioned above burns at once, and a low-temperature-oxidation reaction stops producing it. Moreover, as for an oxidation catalyst component, oxidation capacity increases as temperature generally becomes high. For this reason, when using only an oxidation catalyst component, it will be necessary to supply a reducing agent to a catalyst at temperature quite lower than the temperature which a catalyst activates, and there is an inclination for the operating temperature limits of a catalyst to become narrow. He is trying to reduce the oxidation capacity of an oxidation catalyst component relatively in this invention by making an exhaust air purification catalyst support a reduction catalyst component in addition to an oxidation catalyst component. By this, even if the temperature of a catalyst becomes high, the oxidation capacity as the whole exhaust air purification catalyst does not increase, but it becomes possible to produce the low-temperature-oxidation reaction of a reducing agent also at an elevated temperature comparatively. That is, it is possible by having made exhaust air purification support a reduction catalyst component with this invention in addition to an oxidation catalyst component to generate a reducing-agent radical continuously on a catalyst in a large temperature requirement.

[0015] According to invention according to claim 4, said exhaust air purification catalyst holds the supplied reducing agent in a catalyst, and any 1 term of claim 1 to claim 3 which generates said labile matter continuously on a catalyst is provided with the exhaust air purification approach of a publication by producing the low-temperature-oxidation reaction of said held reducing agent in said predetermined

temperature field under oxygen existence. That is, in invention according to claim 4, the function to hold the supplied reducing agent in a catalyst is given to the exhaust air purification catalyst. This function can be given by using in structure the thing which adsorbs [adsorption or] a hydrocarbon, hydrogen, etc. like the matter which has a hydrogen storing metal alloy and a perovskite structure as catalyst support. By enabling maintenance of a reducing agent in a catalyst, the held reducing agent is gradually emitted in a predetermined temperature field, and it comes to cause a low-temperature-oxidation reaction on a catalyst. For this reason, on a catalyst, the radical of a reducing agent comes to occur continuously.

[0016] The reducing agent which was supplied to an internal combustion engine's flueway according to invention according to claim 5 is held, and it sets to whenever [more than predetermined activation temperature / catalyst temperature], and is NOX under a reduction component and exhaust air under a hyperoxia ambient atmosphere. With possible making it react alternatively By arranging the exhaust air purification catalyst containing an oxidation catalyst component, supplying a reducing agent to this exhaust air purification catalyst, and making more highly than the boiling point of said reduction component whenever [said exhaust air purification catalyst temperature] into a predetermined temperature field lower than said activation temperature under a hyperoxia ambient atmosphere NOX under the labile matter which was made to produce the low-temperature-oxidation reaction which oxidizes without following combustion on said reduction component, and generates the labile matter, and was generated, and engine exhaust air It is made to react and is NOX under exhaust air. The exhaust air purification approach of the internal combustion engine which does reduction purification is offered.

[0017] That is, by using the exhaust air purification catalyst containing an oxidation catalyst component in invention according to claim 5 in the field which the low-temperature-oxidation reaction of a reducing agent produces, the radical of a reducing agent is generated and it is NOX under exhaust air. Reduction purification is carried out. As mentioned above, exhaust air purification catalysts, such as a selection reduction catalyst, are also set under a hyperoxia ambient atmosphere, when whenever [catalyst temperature] is more than activation temperature, and it is NOX under reducing agents, such as a hydrocarbon, and exhaust air. It is made to react alternatively and is NOX. Although it can return, since the reaction of a reducing agent and the oxygen under exhaust air becomes dominant under a hyperoxia ambient atmosphere, it is NOX. The rate of purification becomes low. By maintaining the exhaust air purification catalyst containing an oxidation catalyst component to predetermined temperature in this invention, as a reducing agent is made to produce a low-temperature-oxidation reaction, it also sets under a hyperoxia ambient atmosphere, and it is NOX. The high rate of purification is attained. By generating the labile matter (radical) of a reducing agent on a catalyst continuously by the low-temperature-oxidation reaction of a reducing agent, it also sets under an excess oxygen ambient atmosphere, and they are a radical and NOX. A reaction comes to occur preferentially and it is NOX under exhaust air. It is purified. In addition, at the temperature which an exhaust air purification catalyst activates, since the capacity of an oxidation catalyst component is high and combustion of a reducing agent arises, the above-mentioned predetermined temperature is made into temperature lower than activation temperature. Moreover, since it is hard coming to generate a low-temperature-oxidation reaction while the reducing agent supplied to the exhaust air purification catalyst has been liquefied, it is needed that the above-mentioned predetermined temperature is temperature higher than the boiling point of a reducing agent.

[0018] According to invention according to claim 6, the exhaust air purification approach of the internal combustion engine according to claim 5 which supplies said reducing agent to said exhaust air purification catalyst before said internal combustion engine's starting is offered. That is, in invention according to claim 6, before exhaust air reaches before an internal combustion engine's starting (i.e., an exhaust air purification catalyst), the reducing agent is supplied to the exhaust air purification catalyst. The exhaust air purification catalyst was adsorbed or an exhaust air purification catalyst front-face top will be covered the supplied reducing agent.

[0019] If an engine starts in this condition and exhaust air reaches an exhaust air purification catalyst, whenever [exhaust air purification catalyst temperature] will go up. The reducing agent supplied when the temperature of an exhaust air purification catalyst went into the field which a low-temperature-oxidation reaction produces is evaporated on an exhaust air purification catalyst, and produces a low-temperature-oxidation reaction. Since the reducing agent is supplied to the whole catalyst before engine starting, it will be covered with the radical which produced with the whole catalyst and the whole catalyst front face generated by the low-temperature-oxidation reaction in this case.

[0020] It is the starting back NOX about an engine. The radical generated when the reducing agent was supplied, after the exhaust air to include was supplied to the exhaust air purification catalyst is NOX

immediately. It is reacted and consumed. For this reason, a radical generation rate and NOX It is NOX while have balanced inflow. Although purified by fitness by the radical, since the radical generation rate by the low-temperature-oxidation reaction is comparatively slow, they are once radical formation and NOX. The amounts of the radical which a catalyst will generate if balance with an inflow collapses run short, and it is NOX under exhaust air. A catalyst may be passed while it has been unreacted. Moreover, it is NOX to a catalyst front face. In the condition that oxygen adsorbed, the case where are hard coming to generate and sufficient radical is not generated produces the radical of a reducing agent. In this invention, in order to supply a reducing agent to an exhaust air purification catalyst before exhaust air reaches, at the time of the temperature rise of an exhaust air purification catalyst, the oxygen with which it adsorbed on the catalyst front face during the engine halt reacts with a reducing agent, and is consumed. For this reason, by this invention, the low-temperature-oxidation reaction of a reducing agent comes to arise with the whole catalyst, and it comes to be covered by the radical by which the whole catalyst front face was generated. For this reason, NOX under exhaust air NOX which flows while it is prevented that a catalyst front face is adsorbed Even if fluctuation of an amount arises, the situation where radicals run short does not arise.

[0021] According to invention according to claim 7, said exhaust air purification catalyst supports platinum or palladium as a catalyst component, and the exhaust air purification approach of the internal combustion engine according to claim 5 or 6 which can stick to a catalyst component front face is provided with said generated labile matter. That is, the exhaust air purification catalyst is supporting platinum or palladium with invention according to claim 7 as a catalyst component. Platinum and palladium adsorb the radical which functioned as an oxidation catalyst and was generated good on a front face. Thereby, the radical generated by the low-temperature-oxidation reaction comes to cover a catalyst front face.

[0022] According to invention according to claim 8, any 1 term of claim 5 to claim 7 which generates said labile matter continuously on a catalyst by said low-temperature-oxidation reaction, and supplements a catalyst with the consumed labile matter is provided with the exhaust air purification approach of the internal combustion engine of a publication by performing supply of a reducing agent continuously. That is, in invention according to claim 8, supply of a reducing agent is performed continuously. For this reason, NOX NOX the radical consumed by the reaction is filled up, and the radical of amount always sufficient on a catalyst comes to exist, and according to lack of a radical Decline in the rate of purification does not arise. In addition, with continuous supply of a reducing agent, both the continuation supply which for example, always supplies a little reducing agent to a catalyst continuously, and the intermittent supply which supplies the reducing agent of an initial complement for every time amount of a certain are included.

[0023] According to invention according to claim 9, a liquefied hydrocarbon is used as said reducing agent, and the exhaust air purification approach of the internal combustion engine according to claim 5 which makes said labile matter of the amount of requests generate on a catalyst is offered by changing at least one side of whenever [amount-of-supply / of the reducing agent to a catalyst /, or catalyst temperature] according to the description of a hydrocarbon. That is, in invention according to claim 9, a liquefied hydrocarbon, for example, fuel oil etc., is used as a reducing agent. Moreover, as for a liquefied hydrocarbon, it has become clear that the amount of generation of a hydrocarbon radical changes with the descriptions even if it is the same conditions. For example, in fuel oil with the high cetane number, the amount of generation of a radical is larger than fuel oil with the cetane number low also on the same conditions.

[0024] The amount of generation of the radical on a catalyst is controlled by this invention by changing at least one side of whenever [reducing-agent amount-of-supply and catalyst temperature] according to the description of the reducing agent to supply. For example, when using fuel oil with the low cetane number as a reducing agent, it is prevented that the amount of the radical which will be generated if the fuel oil amount of supply is made to increase compared with the case where fuel oil with the high cetane number is used falls. Moreover, since the amount of radical formation increases with the rise of whenever [catalyst temperature] even if it is the same fuel oil, you may make it raise whenever [catalyst temperature] compared with the case where fuel oil with the high cetane number is used, when using fuel oil with the low cetane number.

[0025] According to invention according to claim 10, the specific constituent concentration under exhaust air after passing said exhaust air purification catalyst is detected, and the exhaust air purification approach of the internal combustion engine according to claim 5 which changes the reducing-agent conditions of supply to said exhaust air purification catalyst according to the concentration of this specific component is offered. That is, in invention according to claim 10, the reducing-agent conditions of supply to an exhaust air purification catalyst are changed according to the specific constituent concentration under exhaust air after

exhaust air purification catalyst passage. Here, as a specific component under exhaust air, it is the reducing-agent radical (for example, aldehyde group) and NOX which are generated with an exhaust air purification catalyst. It is NOX in an exhaust air purification catalyst like a component. The thing showing a purification condition is used. For example, NOX of exhaust air after exhaust air purification catalyst passage Non-purified NOX since there are few amounts of radical formation in exhaust air purification catalyst appearance when concentration is high (or when radical constituent concentration is low) It is thought that it flowed into the downstream. In this case, by increasing the reducing-agent amount of supply to an exhaust air purification catalyst etc., if the amount of radical formation on an exhaust air purification catalyst is increased, it will be non-purified NOX. It can prevent flowing into the downstream. Thereby, it is an engine's NOX. Also when changing the amount of generation, it is always NOX. It becomes possible to maintain purification effectiveness highly.

[0026] According to invention according to claim 11, the possible upstream exhaust air purification catalyst of making the reducing agent supplied to the upstream of said exhaust air purification catalyst in said predetermined temperature field including the oxidation catalyst component produce a low-temperature-oxidation reaction further is arranged, and the exhaust air purification approach of the internal combustion engine according to claim 5 made to become small from the oxidation capacity of the exhaust air purification catalyst of the downstream about the oxidation capacity of this upstream exhaust air purification catalyst is offered.

[0027] That is, in invention according to claim 11, a low-temperature-oxidation reaction generates a radical using the large exhaust air purification catalyst of oxidization capacity arranged to the comparatively small exhaust air purification catalyst of the oxidation capacity arranged to the upstream, and the downstream comparatively. It is NOX that a radical is generated continuously, without the low-temperature-oxidation reaction of a reducing agent arising at a comparatively low rate on a catalyst, and conversion to the radical of a reducing agent arising at once as mentioned above. When raising the rate of purification, it is desirable and, for that, the smaller one of the oxidation capacity of a catalyst is desirable. However, when the rate of the low-temperature-oxidation reaction of a reducing agent is low, the amount which is not converted into a radical among the supplied reducing agents, but flows into the catalyst downstream as it is will increase. In this invention, the low exhaust air purification catalyst of oxidation capacity is comparatively arranged to the upstream, a radical is continuously generated by making a reducing agent produce a low-temperature-oxidation reaction according to this exhaust air purification catalyst, and it is NOX under exhaust air. It purifies at the high rate of purification. On the other hand, it will flow into the downstream, without converting some reducing agents into a radical on an exhaust air purification catalyst in this case. However, it is NOX under exhaust air which the unreacted reducing agent which passed the catalyst of the upstream was adsorbed by the exhaust air purification catalyst of the downstream in the part, converted the remainder into the radical by the low-temperature-oxidation reaction on the exhaust air purification catalyst, and was not purified with the exhaust air purification catalyst of the upstream in this invention since the exhaust air purification catalyst with comparatively high oxidation capacity was arranged at the downstream of an exhaust air purification catalyst. It reacts. For this reason, while emission to the atmospheric air of the reducing agent which flows out of the exhaust air purification catalyst of the upstream is prevented, it is NOX as the whole. Purification effectiveness improves further.

[0028]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is explained. It is NOX under exhaust air by converting the supplied reducing agent (fuel oil) into a hydrocarbon radical with the following operation gestalten. The exhaust air purification catalyst to purify is used. Although this catalyst is similar with an exhaust air purification catalyst well-known about a support component and a configuration, the conventional catalyst functions under completely different conditions, and it is NOX under exhaust air. It is efficient and purifies. For this reason, in the following explanation, in order to distinguish from the conventional exhaust air purification catalyst, the exhaust air purification catalyst used by this invention will be called for convenience a RAP (Radical Active Process) catalyst.

[0029] First, it is NOX of a RAP catalyst to the beginning. A cleaning effect is explained. A RAP catalyst is the selection reduction catalyst which is a catalyst containing oxidation catalyst components, such as platinum (Pt) and palladium (Pd), for example, supported Pt and Pd, or NOX. An occlusion reduction catalyst etc. can be used as a RAP catalyst. These catalysts are used with an anticipated-use method in the field more than the activation temperature (for example, 300 degrees C) to which the oxidation capacity of the supported oxidation catalyst component becomes high. When a reducing agent (fuel oil) is supplied to these oxidation catalyst components by whenever [more than activation temperature / catalyst

temperature], a reducing agent burns on a catalyst and is H_2O and CO_2 . It is converted. On the other hand, with a RAP catalyst, a reducing agent (fuel oil) is supplied in a temperature requirement lower than the activation temperature of an oxidation catalyst component, by producing a low-temperature-oxidation reaction, the intermediate oxide of a hydrocarbon is generated and the radicals (free radical) (for example, an aldehyde system radical, a carboxylic-acid system radical, an alcoholic system radical, etc.) of a hydrocarbon are generated from this intermediate oxide. these radicals -- labile -- high -- NOX etc. -- since it is easy to react especially with the unstable matter chemically -- the bottom of a hyperoxia ambient atmosphere -- also setting -- a reaction with oxygen -- NOX Priority comes to be given to a reaction.

[0030] That is, if hydrocarbon R-H (R is an aldehyde group, a methyl group, etc.) is supplied to a RAP catalyst under a hyperoxia ambient atmosphere, a hydrocarbon will oxidize and an intermediate oxide RO will be generated by the reaction of $R-H+O_2 \rightarrow RO+OH$. This intermediate oxide is further converted into R. (radical) by the reaction of $RO \rightarrow R$. on catalysts (Pt etc.).

[0031] radical R. generated by the above -- NOX(s) (NO , NO_2 , etc.) -- preferential -- reacting -- NOX from -- oxygen -- taking -- oxide RO_2 It generates. That is, it can come $R+NOX \rightarrow RO_2+N_2$, is alike, and NOX more. N_2 It is returned. The intermediate oxide generated since the oxidation capacity of a catalyst was high in this field although the intermediate oxide RO was generated also in oxidation reaction of the hydrocarbon in the field more than the activation temperature of a catalyst oxidizes immediately under existence of oxygen, and is the last oxide RO_2 . Since it becomes, radical R. is not generated in the oxidation reaction (combustion) in the elevated-temperature field of a catalyst.

[0032] Although the reaction which generates above-mentioned hydrocarbon radical R. is called the low-temperature-oxidation reaction on these specifications, a low-temperature-oxidation reaction can be defined as oxidation reaction in the field which becomes smaller than the calorific value of the hydrocarbon with which the heating value generated by the oxidation reaction without combustion of a hydrocarbon or the reaction was supplied. As mentioned above, oxygen is needed for a low-temperature-oxidation reaction for generation of an intermediate oxide. Moreover, it also puts under oxygen existence and the generated radical is NOX actively. It reacts and is NOX. It is high NOX in order to return. The rate of purification can be attained. For this reason, by arranging a RAP catalyst to the flueway where the combustion exhaust air with a larger excess air factor than 1.0 circulates, supplying a reducing agent to a RAP catalyst, and producing a low-temperature-oxidation reaction, the hydrocarbon radical generated on the RAP catalyst is used, and it is NOX under exhaust air. It becomes possible to carry out reduction purification. In this case, at the conventional selection reduction catalyst, it is NOX under oxygen existence. It is low NOX in order to perform a reduction reaction. To having attained only the rate of purification, it also puts under oxygen existence and a hydrocarbon radical is NOX. It is high NOX in order to react preferentially. It becomes possible to attain the rate of purification. Moreover, the conventional NOX NOX absorbed in the occlusion reduction catalyst It is necessary to reduce the excess air factor of the exhaust air which supplies a lot of [in order to carry out reduction purification] reducing agents for a catalyst, and flows into a catalyst or less to 1.0. It is NOX under exhaust air, fixing or more to 1.0 (namely, Lean air-fuel ratio) the excess air factor of the exhaust air which flows with a RAP catalyst catalyst to complicated control of the excess air factor of exhaust air having been needed. There is an advantage whose reduction purification is attained.

[0033] A RAP catalyst is used and it is NOX under exhaust air. In order to purify at high effectiveness, it is necessary to satisfy two conditions, that a low-temperature-oxidation reaction arises and generating [by (2) low-temperature-oxidation reactions / a radical]-continuously **, on (1) catalyst. In order to satisfy these conditions, it is desirable to adjust the temperature of a catalyst, the excess air factor of exhaust air, reducing-agent conditions of supply, etc. to the specific range. Hereafter, these conditions are explained.

[0034] (1) as the condition above-mentioned was carried out whenever [catalyst temperature], without the reducing agent (fuel oil) with which the oxidization capacity of a catalyst was supplied in the high condition burns on a catalyst and it generates a radical -- CO_2 etc. -- it will become the last oxide. For this reason, there must be whenever [catalyst temperature] in the temperature field lower than the activation temperature of a catalyst to which the oxidation capacity of a catalyst becomes comparatively low at least. When whenever [catalyst temperature] is too low, the oxidation reaction itself stops moreover, arising. Moreover, since it will be hard to produce a chemical reaction if the reducing agent supplied to the RAP catalyst is in the condition of a liquid, in the condition that a low-temperature-oxidation reaction arises at least, the reducing agent needs to be evaporated and whenever [catalyst temperature] needs to be higher than the boiling point of the supplied reducing agent. Furthermore, the reducing agent which supplied the radical generation rate when the radical generation rate became excessive although whenever [catalyst temperature] became so large that it is high will be converted at once by the radical also in the temperature

field which a low-temperature-oxidation reaction produces. If the supplied reducing agent is converted at once by the radical, on a catalyst, a reducing agent will be temporarily insufficient and generation of a radical will stop. Although a lot of radicals will be generated on a catalyst at once on the other hand if the supplied reducing agent is converted at once by the radical, this radical does not necessarily remain on a catalyst as it is, and it is NOX. The superfluous radical which was not used for reduction will react with the oxygen under exhaust air, and will be consumed. For this reason, the condition that a radical does not exist temporarily on a catalyst if a radical generation rate, i.e., the rate of a low-temperature-oxidation reaction, is too large arises, and it is NOX. It cannot purify. Therefore, it is necessary to make whenever [catalyst temperature] into the field where the rate of a low-temperature-oxidation reaction becomes comparatively low.

[0035] Namely, the above to NOX It is needed that whenever [for purification / RAP catalyst catalyst temperature] is lower than the activation temperature of an oxidation catalyst component at least, and it is higher than the boiling point of the reducing agent moreover supplied, and it is needed for a low-temperature-oxidation reaction to arise in a further comparatively low reaction rate. Although this temperature field changes also with classes of the catalyst component to be used or reducing agent, in using gas oil as a reducing agent, about 170 degrees C becomes minimum temperature, for example.

[0036] Moreover, when there is an inclination which becomes so low that the oxidation capacity of a catalyst is high and oxidation capacity uses a high catalyst about the upper limit of the above-mentioned temperature field, it becomes low, and it becomes high when oxidation capacity uses a low catalyst. Moreover, also when making the high oxidation catalyst of oxidization capacity support, it is possible by making coincidence support a reduction catalyst component (for example, rhodium (Rh)) with an oxidation catalyst to make high the upper limit of the above-mentioned temperature field.

[0037] That is, since the oxidation capacity of an oxidation catalyst component is controlled by the reduction capacity of a reduction catalyst component by making an oxidation catalyst add and support a reduction catalyst component, the oxidation capacity as the whole catalyst becomes comparatively small also in a hot field. If a catalyst is made to support an oxidation catalyst component and a reduction catalyst component of an amount to which the oxidation capacity by the oxidation catalyst component and the reduction capacity by the reduction catalyst component become almost equivalent especially, it will become possible to expand greatly the upper limit temperature which a low-temperature-oxidation reaction produces. For example, although a low-temperature-oxidation reaction is not produced above activity temperature (300 degrees C) when only oxidation catalyst components, such as Pt and Pd, are made to support, it has become clear by making reduction catalyst components, such as a rhodium (Rh), support with oxidation catalysts, such as Pt and Pd, that the upper limit temperature of a low-temperature-oxidation reaction rises to about 430 degrees C.

[0038] Therefore, NOX The service temperature field of the RAP catalyst for purification becomes about 170 degrees C - about 430 degrees C.

(2) As exhaust air carried out excess-air-factor ****, for the radical formation by the low-temperature-oxidation reaction, oxygen is needed. For this reason, it is necessary to adjust a RAP catalyst to a hyperoxia ambient atmosphere, and 1.0 or more need to be the excess air factor of the exhaust air supplied to a catalyst.

[0039] On the other hand, the reaction rate of a low-temperature-oxidation reaction becomes so high that the oxygen density under exhaust air is high. For this reason, if the oxygen density under exhaust air becomes high too much, the reducing agent supplied for increase of a rate of reaction will be converted at once by the radical, and the problem it becomes impossible to generate a radical continuously like the case where whenever [catalyst temperature] is high will arise. For this reason, it is needed for the excess air factor of exhaust air to be in 1.0 or more specific range. The range of this excess air factor is NOX highest [although it changes with a catalyst, temperature conditions, etc. to be used] when an excess air factor is in the range of 1.0-1.7 with the RAP catalyst which made Pt and Pd support as a result of an experiment. It has become clear that purification effectiveness is acquired.

[0040] Usually, in the case of the Diesel engine, since it is possible for about 1.6 to make it fall as for the excess air factor at the time of operation, the above-mentioned excess air factor has become with the range which can enough be attained also with a Diesel engine.

(3) It is NOX as reducing-agent conditions-of-supply **** was carried out. It is efficient and it is desirable to continue generating a radical on a catalyst continuously with a comparatively low rate of reaction without the supplied reducing agent radical-izing at once, in order to purify. For that, it is desirable to make a reducing agent reach a RAP catalyst in the state of a liquid. It is because the case where the reducing agent

supplied by a reaction progressing rapidly is converted at once by the radical will arise on a catalyst if a reducing agent reaches a catalyst by the gaseous state. If a catalyst is reached while the reducing agent has been liquefied, since it passes the process which a reducing agent evaporates on a catalyst and a low-temperature reaction will be produced, a gas-like reducing agent comes to be supplied to a reducing agent at a comparatively loose rate in process of evaporation. For this reason, by supplying a liquid-like reducing agent, a radical generation rate becomes low and a radical comes to generate continuously by the shape of a catalyst.

[0041] As mentioned above, it is NOX under exhaust air at a RAP catalyst. It is efficient and the conditions for purifying are as follows.

(1) It is more than the boiling point of the reducing agent to supply, and maintain whenever [catalyst temperature] to the temperature (for example, 170 degrees C - 430 degrees C) which a specific low-temperature reaction lower than the activation temperature of the supported oxidation catalyst component produces.

[0042] (2) Maintain the excess air factor of exhaust air in the range (1.0 to about [for example,] 1.7) in which 1.0 or more radical generation rates do not become excessive.

(3) Use the reducing agent of a liquid, and make it reach a catalyst, while the reducing agent has been in a liquid condition.

It is NOX by filling the conditions of (3) with the operation gestalt explained below from the above (1) using a RAP catalyst. High purification effectiveness is attained.

[0043] ** The 1st operation gestalt drawing 1 is drawing explaining the outline configuration of the exhaust emission control device which carries out the 1st operation gestalt of the exhaust air purification approach of this invention. In drawing 1, the flueway where, as for 3, combustion exhaust air of an internal combustion engine, a furnace, etc. flows, and 10 show the RAP catalyst which has been arranged in the flueway 3 and which is mentioned later. With this operation gestalt, the reducing-agent feeder 20 which supplies a liquid reducing agent to the flueway of the upstream of a catalyst 10 is formed.

[0044] The reducing-agent feeder is equipped with the pressurization reducing-agent sources of supply 21, such as a pump and a pressure tank, and the reducing-agent nozzle 23 which injects the reducing agent supplied from a source of supply 21 in the flueway 3 of the catalyst 10 upstream. What 25 shows to drawing 1 is a control valve which adjusts the flow rate of the reducing agent supplied to a nozzle 23 from the pressurization source of supply 21. The fuel oil which the liquid hydrocarbon which evaporates on a catalyst 10 and generates a hydrocarbon as a reducing agent used with this operation gestalt is used, for example, is comparatively hard to evaporate, such as kerosene and gas oil, is used. The reducing-agent nozzle 23 is arranged in the location which approached the catalyst 10 so that a catalyst 10 might be reached, while it had been liquefied, without the injected fuel oil exhausting and evaporating.

[0045] The RAP catalyst used with this operation gestalt should be supported by the porosity zeolite (for example, ZSM5 grade) in oxidation catalyst components, such as platinum (Pt) and palladium (Pd), and is considered as the same configuration as the selection reduction catalyst of a general Pt/Pd system.

Moreover, as for the combustion exhaust air which circulates to a flueway 3, the combustion condition of an internal combustion engine or a furnace is adjusted so that an excess air factor may become the range of 1.0-1.7. Moreover, the exhaust-gas temperature in catalyst 10 inlet port is higher than the boiling point (for example, 170 degrees C) of the reducing agent supplied, and distance with exhaust air generation sources, such as a catalyst 10, an internal combustion engine, or a furnace, is set up so that it may become the temperature requirement lower than the activation temperature (for example, about 300 degrees C) of the oxidation catalyst component of a catalyst 10 which the low-temperature-oxidation reaction of a reducing agent produces on a catalyst 10.

[0046] The flow rate of the reducing agent injected from a nozzle 23 is controlled by this operation gestalt by adjusting the opening of a control valve 25 with the control units 30, such as a microcomputer. The reducing-agent injection quantity from a nozzle 23 is controlled according to the exhaust air flow rate and NOX concentration which flow a flueway 3. The reducing agent injected from the nozzle 23 reaches a catalyst 10, while it has been liquefied, and it evaporates comparatively gently on a catalyst 10. NOX which the radical which it was converted into the radical through the intermediate oxide RO, and the reducing agent evaporated on the catalyst generated is exhausting since the exhaust-gas temperature and the excess air factor are adjusted with this operation gestalt in the range which a low-temperature-oxidation reaction produces on a catalyst as mentioned above It is NOX under exhaust air by reacting preferentially. It is efficient and is purified.

[0047] In addition, injection of the reducing agent from a nozzle 23 may be performed continuously, and

injection intermittent in the shape of a pulse may be performed. With this operation gestalt, since the support of a catalyst 10 is adsorbed, and some reducing agents supplied also when a reducing agent was injected intermittently since the catalyst support which can adsorb a hydrocarbon was used invade from support after that and it produces a low-temperature-oxidation reaction, on a catalyst 10, a radical continues and it continues being generated [come].

[0048] Moreover, although only oxidation catalysts, such as Pt and Pd, are supported with this operation gestalt on a catalyst 10, if it makes reduction catalyst components, such as Rhodium Rh, support on a catalyst 10 in addition to these oxidation catalysts and is made for the oxidation capacity of components, such as Pt and Pd, and the reduction capacity of components, such as Rh, to serve as an abbreviation EQC as a whole, it will be NOX high also in a further hot field. It becomes possible to maintain purification effectiveness.

[0049] ** The 2nd operation gestalt drawing 2 is drawing explaining the outline configuration of the exhaust emission control device which carries out the 2nd operation gestalt of the exhaust air purification approach of this invention. With this operation gestalt, the same RAP catalyst 10 as the 1st operation gestalt is arranged to an internal combustion engine's (this operation gestalt Diesel engine) 1 flueway 3.

[0050] It is the reducing-agent feeder equipped with the 1st the same reducing-agent nozzle 23 as an operation gestalt, control valve 25, and reducing-agent source of supply 21 which 20 shows to drawing 2 . With this operation gestalt, the diesel fuel oil same as a reducing agent as the fuel for an engine 1 is used. Furthermore, with this operation gestalt, the conveyance air supply equipment 40 which injects air is formed in the upstream of the reducing-agent nozzle 23. Conveyance air supply equipment 40 equips the air nozzle 41 arranged in the flueway 3 of the upstream of the reducing-agent nozzle 23, and the nozzle 41 with the sources 43 of pressurization air supply which can supply pressurization air before engine starting, such as an electric air pump and an air tank.

[0051] With this operation gestalt, a reducing agent is supplied to a catalyst 10 before engine 1 starting (after a main switch is turned ON until engine starting actuation is performed). That is, if it detects that an engine's 1 ignition key was inserted, a control device 30 will start the electric air pump 43, and will supply air all over a flueway 3 from an air nozzle 41. The airstream which flows through a catalyst 10 in a flueway 3 by this air arises. Moreover, a control circuit 30 opens a control valve 25 to coincidence, and injects fuel oil from the reducing-agent nozzle 23 to it. Thereby, the fuel oil injected from the reducing-agent nozzle 23 rides on the conveyance airstream produced by the air injected from the air nozzle 41, reaches a catalyst 10, and adheres to the front face of a catalyst 10. A control circuit 30 puts an engine 1 into operation, after only the time amount defined beforehand performs air injection from an air nozzle 41, and fuel oil injection from the reducing-agent nozzle 23. Here, time amount which performs fuel oil injection is made into time amount required to cover the whole catalyst 10 front face with the fuel oil injected from the nozzle 23, and is defined by experiment etc.

[0052] Thereby, where the whole catalyst 10 front face is covered with a reducing agent, an engine 1 starts. With this operation gestalt, an engine's 1 fuel oil consumption is set up so that Diesel engine 1 may be operated with an excess air factor (it is about 1.6 at an excess air factor) lower than usual. Moreover, the catalyst 10 is arranged in the location which does not exceed the upper limit of the temperature requirement which the low-temperature-oxidation reaction which the exhaust-gas temperature which usually reaches a catalyst 10 at the time of operation mentioned above produces.

[0053] If an engine 1 starts and an engine's exhaust air comes to reach a catalyst 10, the temperature of a catalyst 10 will become the temperature field which it goes up and the low-temperature-oxidation reaction of the reducing agent mentioned above produces. At this time, the reducing agent (fuel oil) which covered all the front faces of a catalyst 10 starts evaporation. Moreover, since it has become about 1.6, if the temperature of a catalyst 10 becomes the temperature field which a low-temperature-oxidation reaction produces, the excess air factor of exhaust air of an engine 1 is adsorbed in the radical which fuel oil produced the low-temperature-oxidation reaction with the whole catalyst 10, came to generate a radical gradually, and was generated on catalyst component front faces, such as Pt and Pd, by the catalyst 10 whole, and its catalyst component front face will be radical, and it will come to be covered. This radical is NOX under exhaust air. It reacts and is NOX. It is consumed purifying. For this reason, if supply of the reducing agent to a catalyst 10 is kept stopped after engine starting, the reducing agent supplied before starting will be consumed soon, and the condition that the radical does not adsorb on the catalyst 10 front face will produce it. In the condition that a radical does not exist in catalyst 10 front face, it is oxygen and NOX under exhaust air. Catalyst component front faces, such as Pt and Pd, will be adsorbed, and in this part, even if it supplies a reducing agent, a radical becomes is hard to be generated.

[0054] For this reason, after an engine starts, the reducing agent from the reducing-agent nozzle 23 is supplied continuously, and he is trying to always adsorb the whole catalyst 10 front face in a radical with this operation gestalt. The injection quantity of the reducing agent from the nozzle 23 after engine starting is NOX at a catalyst 10. It considers as the amount which can fill up the amount of the radical consumed by the reaction. Thereby, on a catalyst 10, it is NOX. The reducing agent which generates the radical of the amount of a radical and the amount of an abbreviation EQC consumed by the reaction comes to be supplied, and the condition of the whole catalyst front face having always been radical, and having been covered comes to continue.

[0055] Thus, when a radical continues the condition of having adsorbed, on the whole catalyst 10 front face, it is NOX under exhaust air by change of for example, an engine service condition. Since the amount of a radical can fully be secured even when concentration increases somewhat, lack of a radical arises by fluctuation of a service condition etc., and it is non-purified NOX. Flowing out is prevented. In addition, also in this operation gestalt, injection of the reducing agent from the reducing-agent nozzle 23 may be continuous, and may be intermittently performed in the shape of a pulse.

[0056] ** With the 3rd operation gestalt book operation gestalt, according to the description of a reducing agent, engine operational status and the reducing-agent amount of supply are changed using the equipment of the same configuration as drawing 2 during operation of an engine 1, and the radical of the specified quantity is always generated on a catalyst 10. Even if the amount of generation of the radical in a RAP catalyst (generation rate) has the same conditions, such as temperature conditions and the amount of supply of an oxygen density and a reducing agent, it changes with the descriptions of a reducing agent. For example, it has become clear that the amount of generation of a radical is so large that the cetane number of fuel oil is high when supplying a diesel fuel oil as a reducing agent also on the same conditions.

[0057] For this reason, the amount of the radical generated on a catalyst 10 when the reducing agent was supplied on the same conditions and what has the cetane number low as a fuel for an engine 1 is used is insufficient, and it is non-purified NOX. It may flow into the catalyst downstream. Then, he detects the cetane number of a use fuel and is trying to change reaction conditions, such as whenever [catalyst temperature], and the reducing-agent amount of supply, with this operation gestalt according to the cetane number by acting as the monitor of an engine's 1 combustion chamber internal pressure.

[0058] First, the cetane number detection approach of the use fuel by combustion chamber internal pressure is explained. Drawing 3 is drawing showing typically the pressure variation which can be set like the compression stroke and explosion line of a combustion chamber of a Diesel engine. If combustion chamber internal pressure rises by rise of a piston in a compression stroke and a fuel is injected near a compression stroke top dead center (drawing 3 , A point) in drawing 3 , combustion chamber internal pressure will go abruptly up near a top dead center by combustion of a fuel. The combustion chamber internal pressure in a compression stroke rises smoothly until a fuel is injected, as shown in drawing 3 .

[0059] In the Diesel engine, since it is few, the temperature of combustion indoor air is low and the temperature rise by compression has not reached the ignition temperature of a fuel, even if the early stage of a compression stroke performs fuel injection at a compression stroke early stage, a combustion chamber should not be produced, but as a continuous line originally shows to drawing 3 , the pressure should rise smoothly. However, if a little fuel is injected in fact at a compression stroke early stage (for example, drawing 3 , a B point), as a dotted line shows to drawing 3 , the pressure after injection will rise temporarily. However, the pressure which rose temporarily since combustion was not produced in this case, either comes to be in agreement with the pressure variation at the time of an after that usual compression stroke (continuous line).

[0060] The hydrocarbon component of the shape of a straight chain with the low cetane number included in fuel oil oxidizes, an intermediate oxide RO is formed, and the reason a pressure rises temporarily when fuel injection is performed at a compression stroke early stage, after injecting like drawing 3 is considered that a temporary pressure buildup arises with the heat of reaction in that case. Moreover, since the above-mentioned reaction becomes active so that the cetane number of fuel oil is so high that many hydrocarbon components with the low cetane number are contained in a fuel, the difference (drawing 3 , ΔP) of the pressure in the usual compression stroke and the peak of the pressure buildup after the fuel injection of a compression stroke early stage becomes so large that the cetane number of fuel oil is high. For this reason, this differential pressure ΔP can be used as an index showing the cetane number of fuel oil.

[0061] With this operation gestalt, the combustion room pressure sensor which can detect combustion chamber internal pressure in an engine's 1 specific gas column is arranged, during operation of an engine, periodically, for cetane number measurement, a little fuel is injected at the early stage of a gas column

compression stroke, and the peak value of a subsequent pressure buildup is detected. And difference ΔP of this peak value and the combustion chamber internal pressure of the coincidence term in the usual compression stroke is computed, and the cetane number of a use fuel is presumed.

[0062] Moreover, with this operation gestalt, a control circuit 30 adjusts the reaction condition in a catalyst 10 so that the radical of an initial complement may always be generated on a catalyst 10 based on the cetane number presumed by the above. For example, when the cetane number of a use fuel is low, the amount of generation of the radical on a catalyst falls. For this reason, a control circuit 30 prevents the fall of the amount of generation of the radical on a catalyst by increasing the reducing-agent injection quantity from the reducing-agent nozzle 23. NOX by change of the description of the reducing agent which this uses Decline in the rate of purification is prevented.

[0063] In addition, the generation rate of the radical in a catalyst 10 becomes so large that whenever [catalyst temperature] is high. For this reason, when the cetane number of a use fuel is low, you may make it raise the exhaust-gas temperature which an engine's load conditions are changed and reaches a catalyst. Moreover, the radical generation rate in a catalyst 10 becomes so large that the oxygen density of exhaust air is high. For this reason, when the cetane number of a use fuel is low, the fuel oil consumption to an engine is reduced and you may make it raise the excess air factor of exhaust air.

[0064] ** As the 4th carried out the operation gestalt above-mentioned, the amount of generation of the radical on a RAP catalyst changes according to whenever [catalyst temperature], and an ambient atmosphere oxygen density. However, when the RAP catalyst has been arranged to an internal combustion engine's flueway, since whenever [catalyst temperature], and an ambient atmosphere oxygen density will become settled with an exhaust-gas temperature and the excess air factor of exhaust air, if an exhaust-gas temperature and an excess air factor change with change of engine operational status etc., according to it, the amount of radical formation on a catalyst will change. Moreover, the amount of generation of the radical on a catalyst is NOX under exhaust air. It is necessary to adjust according to an amount.

[0065] Then, while preventing fluctuation of the amount of radical formation by change of an engine service condition by changing the reducing-agent conditions of supply to a catalyst according to change of the conditions (for example, an exhaust-gas temperature, an excess air factor) which govern the amount of radical formation, he is trying to control the amount of radical formation on a catalyst by this operation gestalt according to the amount of NOX(s) under exhaust air. Drawing 4 is drawing showing the outline configuration of the exhaust emission control device which carries out the 4th operation gestalt of the exhaust air purification approach of this operation gestalt. In drawing 4, the same reference mark as drawing 3 shows the same element as the thing of drawing 3.

[0066] With this operation gestalt, the oxygen density sensor 31 which can measure the oxygen density under exhaust air is arranged at the reducing-agent nozzle 23 upstream of a flueway 3. Moreover, NOX under the temperature sensor 33 which detects an exhaust-gas temperature in the flueway of the RAP catalyst 10 downstream, and exhaust air NOX which detects concentration The sensor 35 is arranged. Control circuits 30 are the exhaust-gas temperatures T and NOX inputted from the oxygen density C and temperature sensor 33 which are inputted from the oxygen density sensor 31. NOX inputted from a sensor 35 Concentration CNOX is supervised for every fixed time amount, and they are the oxygen density C and exhaust-gas temperatures T and NOX from last time. Concentration CNOX Variation ΔC and ΔT and $\Delta CNOX$ While computing, based on such variation, the injection quantity of the reducing agent from the reducing-agent nozzle 23 is controlled.

[0067] For example, when exhaust air oxygen density variation ΔC is forward, since the amount of radical formation on a catalyst 10 is in an increase inclination, a control circuit 30 decreases the reducing-agent injection quantity from the reducing-agent nozzle 23 a constant rate every, as long as ΔC is a forward value. Moreover, on the contrary, when ΔC is a negative value, since the amount of radical formation on a catalyst 10 is decreasing, a control circuit 30 increases the reducing-agent injection quantity from the reducing-agent nozzle 23 a constant rate every, as long as ΔC is a negative value.

[0068] Moreover, when amount of exhaust air temperature changes ΔT is a forward value similarly, the amount of radical formation is in an increase inclination, and when ΔT is a negative value, the amount of radical formation is decreasing. For this reason, a control circuit 30 decreases the reducing-agent injection quantity a constant rate every, as long as the value of ΔT is forward, and as long as it is a negative value, it increases the reducing-agent injection quantity a constant rate every. Moreover, NOX Concentration variation $\Delta CNOX$ When it is a forward value, it is NOX under engine exhaust air. Since it means that radicals ran short on the catalyst 10 for the amount having increased etc., it is necessary to increase the amount of radical formation on a catalyst 10 as quickly as possible. Then, a control circuit 30 is $\Delta CNOX$

about the reducing-agent injection quantity in this case. It is made only for a proportional amount to increase.

[0069] Thus, exhaust air NOX of an exhaust-gas temperature, an exhaust air oxygen density, and the catalyst 10 downstream By controlling the reducing-agent injection quantity according to concentration, it becomes possible to always generate the radical of optimum dose on a catalyst 10, and is NOX which is not purified by lack of a radical. Flowing into the catalyst downstream is prevented. in addition -- this operation gestalt -- exhaust air NOX of the catalyst 10 downstream although control which adjusts the reducing-agent injection quantity according to concentration is performed -- exhaust air NOX concentration -- in addition -- or exhaust air NOX concentration may detect the radical constituent concentration under exhaust air of the catalyst 10 downstream (for example, aldehyde concentration), and control which adjusts the reducing-agent injection quantity according to radical constituent concentration may be performed. That is, the amount of radicals on a catalyst is NOX. If it is in the inclination which run short to an amount, the amount of the radical component which flows into the catalyst downstream will decrease. For this reason, when the radical constituent concentration of catalyst 10 downstream exhaust air decreases, it becomes possible to always generate the radical of optimum dose on a catalyst 10 also by performing control which increases the reducing-agent injection quantity.

[0070] ** The 5th operation gestalt drawing 5 is drawing explaining the outline configuration of the exhaust emission control device which carries out the 5th operation gestalt of the exhaust air purification approach of this invention. In drawing 5, the same reference mark as drawing 2 shows the same element. Also in this operation gestalt, the exhaust air purification catalyst 10 which consists of the same RAP catalyst as drawing 2 is arranged on an engine's 1 flueway 3. However, the point that another RAP catalyst (upstream exhaust air purification catalyst) 15 is arranged is different from the flueway 3 of the downstream of the reducing-agent nozzle 23 by the upstream of the exhaust air purification catalyst 10 with this operation gestalt.

[0071] Oxidation components, such as Pt and Pd, are supported like the exhaust air purification catalyst 10 (downstream exhaust air purification catalyst), and the upstream exhaust air purification catalyst 15 of this operation gestalt can produce the low-temperature-oxidation reaction of a reducing agent like the downstream exhaust air purification catalyst 10. However, the upstream exhaust air purification catalyst 15 of this operation gestalt is using support, such as an alumina, and the point of not having the function which adsorbs the supplied reducing agent and is held is different from the downstream exhaust air purification catalyst 10. Moreover, the amount of support of oxidation components, such as Pt of the upstream exhaust air purification catalyst 15 and Pd, is made fewer than the downstream exhaust air purification catalyst 15, and the oxidation capacity of the upstream exhaust air purification catalyst 15 is small from the oxidation capacity of the downstream exhaust air purification catalyst 10.

[0072] Also in this operation gestalt, Diesel engine 1 is operated with a comparatively low excess air factor (about [for example,] 1.6), and catalysts 10 and 15 are arranged in the location where the exhaust-gas temperature which reaches during engine operation at a catalyst does not exceed the upper limit temperature which the low-temperature-oxidation reaction of a reducing agent produces in catalysts 10 and 15. Also in this operation gestalt, a liquid-like reducing agent (diesel fuel oil) is injected from the reducing-agent nozzle 23 of the reducing-agent feeder 20 during engine operation. The injected reducing agent is NOX under exhaust air by the radical which produced the low-temperature-oxidation reaction on the upstream exhaust air purification catalyst 15, and was generated on the catalyst. Reduction purification is carried out. With this operation gestalt, the amount of catalyst components is set up so that the oxidation capacity of the upstream exhaust air purification catalyst 15 may become small compared with the downstream exhaust air purification catalyst 10. As mentioned above, in order for a low-temperature-oxidation reaction to generate a radical continuously on a catalyst, the smaller one of the oxidation capacity of a catalyst is desirable. For this reason, on the low upstream exhaust air purification catalyst 15 of oxidization capacity, a radical is generated continuously and the rate of purification of NOX becomes high.

[0073] However, it is NOX by having set up small the oxidation capacity of the upstream exhaust air purification catalyst 15 with this operation gestalt. Since the oxidation capacity of what can raise the rate of purification is small, with the upstream exhaust air purification catalyst 15, the amount of the reducing agent which passes a catalyst 15, without oxidizing among the supplied reducing agents will increase. if what has the same hydrocarbon adsorption capacity force as the downstream exhaust air purification catalyst 10 as an upstream exhaust air purification catalyst 15 is used, although this problem will be prevented to some extent, since some hydrocarbons flow into the downstream also in such a case -- exhaust air -- there is a possibility that aggravation of description may arise.

[0074] So, with this operation gestalt, without giving the adsorption capacity force of a hydrocarbon to the

upstream exhaust air purification catalyst 15, an unreacted hydrocarbon purifies exhaust air according to the exhaust air purification catalyst 10 prepared in the downstream, as the whole quantity flows into the downstream. That is, it flows into the downstream exhaust air purification catalyst 10 with this operation gestalt, without comparatively a lot of hydrocarbons reacting with the upstream exhaust air purification catalyst 15. The hydrocarbon which reached the downstream exhaust air purification catalyst 10 since the temperature oxygen conditions which a low-temperature-oxidation reaction produces also in the downstream exhaust air purification catalyst 10 were satisfied with this operation gestalt is NOX under exhaust air with which it was converted into the radical and a part was not purified with the upstream exhaust air purification catalyst 15. It returns. Moreover, a part oxidizes on the large downstream exhaust air purification catalyst 10 of oxidation capacity among the remaining parts of a hydrocarbon, and adsorption maintenance of the hydrocarbon which does not oxidize is carried out at the downstream exhaust air purification catalyst 10. For this reason, at this operation gestalt, it is NOX. While raising the rate of purification further, it is possible to prevent atmospheric-air emission of an unreacted hydrocarbon nearly completely.

[0075]

[Effect of the Invention] It is high NOX, without performing actuation of adjusting the exhaust air air-fuel ratio which flows into a catalyst to a rich air-fuel ratio according to invention given in each claim. The common effectiveness of becoming possible to attain purification effectiveness is done so.

[Translation done.]

* NOTICES *

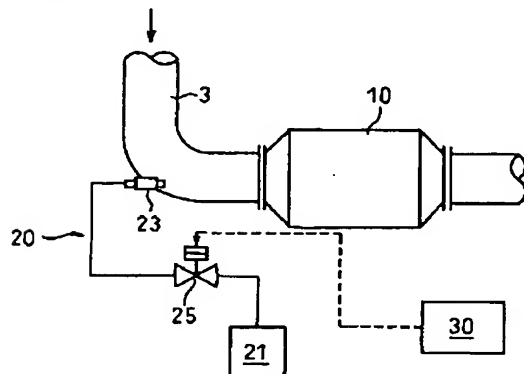
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3. In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

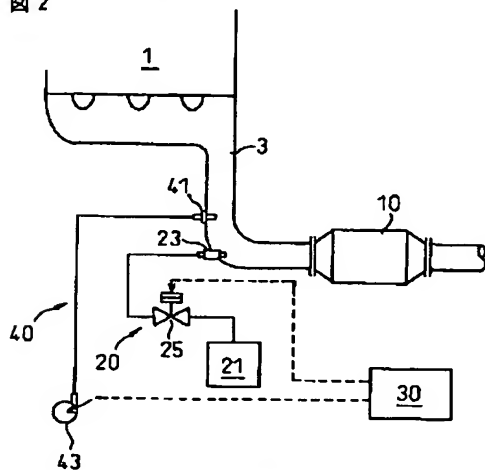
図 1



3...排気通路
10...排気浄化触媒 (RAP触媒)
20...還元剤供給装置
30...制御装置

[Drawing 2]

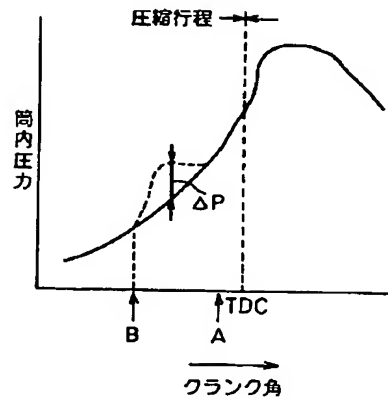
図 2



1...ディーゼル機関
10...排気浄化触媒 (RAP触媒)
20...還元剤供給装置
30...制御装置
40...送気供給装置

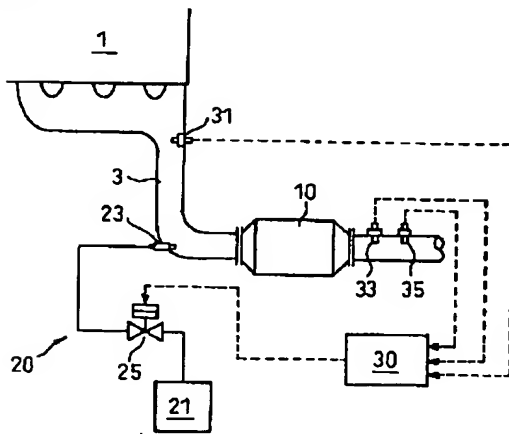
[Drawing 3]

図 3



[Drawing 4]

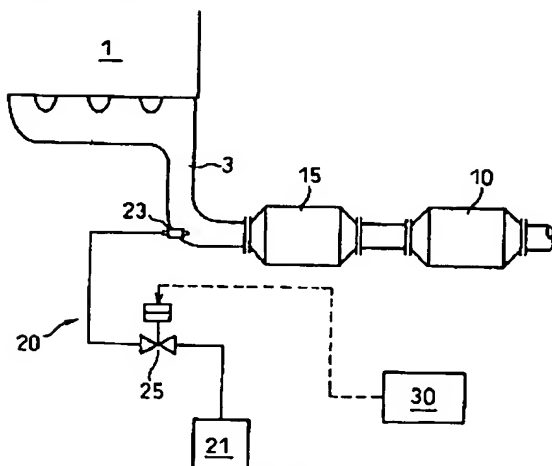
図 4



- 1…ディーゼル機関
- 10…排気浄化触媒 (RAP触媒)
- 20…還元剤供給装置
- 30…制御装置
- 31…酸素濃度センサ
- 33…温度センサ
- 35…NO_xセンサ

[Drawing 5]

図 5



- 1…ディーゼル機関
- 3…排気通路
- 10, 15…排気浄化触媒 (RAP触媒)
- 20…還元剤供給装置
- 30…制御装置

[Translation done.]

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開2000-257419

(P2000-257419A)

(43)公開日 平成12年9月19日(2000.9.19)

(51)Int.Cl. ⁷	識別記号	F I	テリトリー(参考)
F 0 1 N 3/24		F 0 1 N 3/24	L 3 G 0 9 1
B 0 1 D 53/86	Z A B	B 0 1 J 29/22	A 4 D 0 4 8
53/94		F 0 1 N 3/08	B 4 G 0 6 9
B 0 1 J 29/22		3/10	A
F 0 1 N 3/08		3/20	D

審査請求 未請求 請求項の数11 O L (全 13 頁) 最終頁に続く

(21)出願番号 特願平11-55554

(22)出願日 平成11年3月3日(1999.3.3)

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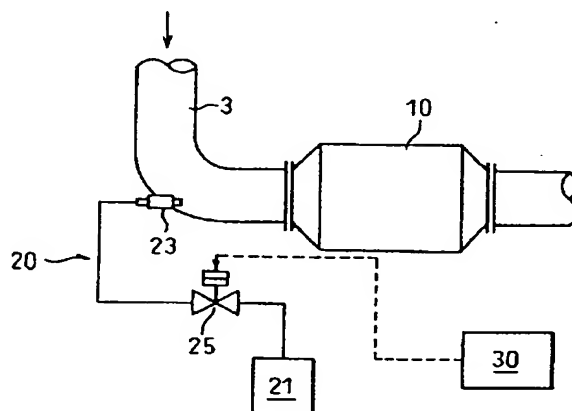
(54)【発明の名称】 排気浄化方法及び装置

(57)【要約】

【課題】 排気空燃比をリッチ空燃比に調整することなく高いNO_x 浄化効率を達成する。

【解決手段】 酸化触媒成分を含み、触媒成分活性化温度より低い所定の温度領域において還元剤を酸素の存在下において燃焼を伴わずに酸化して継続的に還元剤のラジカルを生成する排気浄化触媒を排気通路に配置し、この排気浄化触媒を上記所定温度領域に維持しつつ触媒に還元剤を供給して還元剤ラジカルを生成し、同時にこの排気浄化触媒に空気過剰率が1.0以上の燃焼排気を供給する。触媒上で生成された還元剤ラジカルは酸素過剰雰囲気においても優先的に排気中のNO_x と反応するため、排気空燃比をリッチ空燃比に調整することなく排気中のNO_x が高い浄化効率で還元浄化される。

図 1



3…排気通路
10…排気浄化触媒 (RAP触媒)
20…還元剤供給装置
30…制御装置

【特許請求の範囲】

【請求項 1】 酸化触媒成分を含み、所定の温度領域より高い温度領域では供給された還元剤を酸素の存在下において燃焼させ、前記所定の温度領域では供給された還元剤を酸素の存在下において燃焼を伴わずに酸化して継続的に反応活性物質を生成する低温酸化反応を行う排気浄化触媒を排気通路に配置し、

前記排気浄化触媒を前記所定の温度領域に維持しつつ排気浄化触媒に還元剤を供給することにより還元剤の前記低温酸化反応を生じさせ継続的に前記反応活性物質を生成し

前記排気浄化触媒に空気過剰率が 1.0 以上の燃焼排気を供給し、前記排気浄化触媒上で生成した前記反応活性物質と排気中の NO_x とを反応させて排気中の NO_x を還元浄化する排気浄化方法。

【請求項 2】 前記排気浄化触媒に供給する燃焼排気の空気過剰率を 1.0 以上かつ 1.7 以下とする請求項 1 に記載の排気浄化方法。

【請求項 3】 前記排気浄化触媒は、酸化触媒成分と還元触媒成分とをそれぞれ酸化触媒成分による酸化能力と還元触媒成分による還元能力とがほぼ同等になる量だけ含む請求項 1 または請求項 2 に記載の排気浄化方法。

【請求項 4】 前記排気浄化触媒は供給された還元剤を触媒内に保持し、酸素存在下の前記所定温度領域において、前記保持した還元剤の低温酸化反応を生じさせることにより触媒上に継続的に前記反応活性物質を生成する請求項 1 から請求項 3 のいずれか 1 項に記載の排気浄化方法。

【請求項 5】 内燃機関の排気通路に、供給された還元剤を保持し所定の活性化温度以上の触媒温度において酸素過剰雰囲気下で還元成分と排気中の NO_x とを選択的に反応させることが可能な、酸化触媒成分を含む排気浄化触媒を配置し、

該排気浄化触媒に還元剤を供給し酸素過剰雰囲気下で前記排気浄化触媒温度を前記還元成分の沸点より高く、かつ前記活性化温度より低い所定の温度領域にすることにより、前記還元成分に燃焼を伴わずに酸化して反応活性物質を生成する低温酸化反応を生じさせ、生成した反応活性物質と機関排気中の NO_x とを反応させ排気中の NO_x を還元浄化する内燃機関の排気浄化方法。

【請求項 6】 前記内燃機関の始動前に前記排気浄化触媒に前記還元剤を供給する請求項 5 に記載の内燃機関の排気浄化方法。

【請求項 7】 前記排気浄化触媒は白金またはパラジウムを触媒成分として担持し、生成した前記反応活性物質を触媒成分表面に吸着可能である請求項 5 または請求項 6 に記載の内燃機関の排気浄化方法。

【請求項 8】 還元剤の供給を継続して行うことにより前記低温酸化反応により前記反応活性物質を触媒上に継続的に生成し、消費された反応活性物質を触媒に補充す

る請求項 5 から請求項 7 のいずれか 1 項に記載の内燃機関の排気浄化方法。

【請求項 9】 前記還元剤として液状炭化水素を使用し、炭化水素の性状に応じて触媒への還元剤の供給量または触媒温度の少なくとも一方を変化させることにより触媒上で所望量の前記反応活性物質を生成させる請求項 5 に記載の内燃機関の排気浄化方法。

【請求項 10】 前記排気浄化触媒を通過後の排気中の特定成分濃度を検出し、該特定成分の濃度に応じて前記排気浄化触媒への還元剤供給条件を変化させる請求項 5 に記載の内燃機関の排気浄化方法。

【請求項 11】 更に、前記排気浄化触媒の上流側に、酸化触媒成分を含み前記所定の温度領域において供給された還元剤に低温酸化反応を生じさせることの可能な上流側排気浄化触媒を配置し、該上流側排気浄化触媒の酸化能力を下流側の排気浄化触媒の酸化能力より小さくするようにした請求項 5 に記載の内燃機関の排気浄化方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は排気浄化方法に関し、詳細には空気過剰率が 1 より高いリーン空燃比排気中の NO_x を浄化する排気浄化方法に関する。

【0002】

【従来の技術】空気過剰率が 1 より高い、すなわち酸素過剰雰囲気（リーン空燃比）の排気中の NO_x の浄化に用いられる排気浄化触媒としては、 NO_x 吸蔵還元触媒や選択還元触媒が知られている。 NO_x 吸蔵還元触媒は、アルミナ等の担体上にバリウム（Ba）等の成分と、白金（Pt）のような貴金属とを担持したもので、流入する排気ガスの空燃比がリーンのときに、排気中の NO_x （ NO_2 、 NO ）を硝酸イオン NO_3^- の形で吸収し、流入排気ガスの酸素濃度が低下すると吸収した NO_3^- を放出する NO_x の吸放出作用を行う。例えば、リーン空燃比の排気を NO_x 吸蔵還元触媒に供給すると排気中の NO_x は NO_2 吸蔵還元触媒に吸収され NO_x が排気から除去される。また、 NO_x を吸収した NO_x 吸蔵還元触媒に炭化水素等の還元剤を供給すると供給された還元剤が NO_x 吸蔵還元触媒上で酸化して NO_x 吸蔵還元触媒の雰囲気酸素濃度が低下する。これにより、 NO_x 吸蔵還元触媒からは NO_x が放出され、排気中の還元剤により NO_x 吸蔵還元触媒上で還元浄化される。

【0003】また、選択還元触媒は、例えばゼオライトに触媒成分として、銅（Cu）をイオン交換等により、或いは白金（Pt）を含浸などにより担持させた物が用いられる。選択還元触媒は排気空燃比がリーンのときに、適量の HC 、 CO 等の存在下で NO_x を HC 、 CO と選択的に反応させることにより、排気中の NO_x を還元して N_2 に転換する機能を有している。すなわち、選択還元触媒では、流入する排気中に炭化水素（HC）等

の成分が存在すると、これらHC成分等がゼオライトの細孔に吸着される。また、選択還元触媒の白金、銅等の金属成分にはリーン空燃比下で排気中の NO_x 成分が吸着される。そして、ゼオライトに吸着されたHC等の成分は一定の温度範囲で表面に侵出し白金、銅等の表面に吸着された NO_x と優先的に反応し NO_x が還元浄化される。

【0004】このような排気浄化触媒を用いた排気浄化装置の例としては、例えば特開平4-330314号公報に記載されたものがある。同公報の装置は、ディーゼル機関の排気通路に銅-ゼオライトを使用した選択還元触媒を配置し、触媒上流側の排気通路に還元剤としての燃料を噴射する手段を設けている。同公報の装置では、選択還元触媒が活性化温度（活性化温度）以上の温度領域で機関排気中の炭化水素濃度に応じて排気通路に噴射する燃料量を制御して、選択還元触媒に常に適量の酸素が供給されるようにしている。これにより、ディーゼル機関からのリーン空燃比排気中の NO_x が選択還元触媒に吸着された炭化水素成分により還元浄化される。

【0005】

【発明が解決しようとする課題】ところが、上記公報の装置のように選択還元触媒を用いてリーン空燃比の排気中で選択還元触媒に還元剤を供給して排気中の NO_x を浄化する場合には NO_x の高い浄化率が得られない問題がある。これは、選択還元触媒に担持される白金、銅等は酸化触媒として機能するため、酸素過剰雰囲気では炭化水素成分は NO_x よりも酸素と反応を生成してしまうからである。つまり、リーン空燃比排気中で選択還元触媒に還元剤を供給すると、供給された（或いは選択還元触媒から侵出した）炭化水素はその大部分が触媒上で燃焼して H_2 、 O と CO を形成してしまうため炭化水素と NO_x との反応が生じにくくなり、高い NO_x 浄化率を得ることはできない。

【0006】一方、 NO_x 吸蔵還元触媒を用いた場合には、 NO_x の放出と還元浄化とは還元雰囲気（リッチ空燃比）中で行われるため選択還元触媒に比較して高い NO_x の浄化率を得ることができる。しかし、 NO_x 吸蔵還元触媒から NO_x を放出させ、還元浄化するためには NO_x 吸蔵還元触媒に流入する排気の空気過剰率を1.0より低く（リッチ空燃比に）する必要がある。このため、 NO_x 吸蔵還元触媒から NO_x を放出させるべきときには、例えば通常時にリーン空燃比運転を行うガソリン機関等では一時的に機関をリッチ空燃比運転に切り換えたり、リッチ空燃比運転が困難なディーゼル機関等では多量の還元剤を排気通路に供給すること等により、 NO_x 吸蔵還元触媒に流入する排気の空燃比を一時的にリッチ空燃比に調整する煩雑な操作が必要となる問題があった。

【0007】本発明は、上述した従来の排気浄化触媒の問題に鑑み、排気空燃比をリッチ空燃比に調整すると

となく、しかも高い NO_x 浄化効率を達成可能な排気浄化方法を提供することを目的としている。

【0008】

【課題を解決するための手段】請求項1に記載の発明によれば、酸化触媒成分を含み、所定の温度領域より高い温度領域では供給された還元剤を酸素の存在下において燃焼させ、前記所定の温度領域では供給された還元剤を酸素の存在下において燃焼を伴わずに酸化して継続的に反応活性物質を生成する低温酸化反応を行う排気浄化触媒を排気通路に配置し、前記排気浄化触媒を前記所定の温度領域に維持しつつ排気浄化触媒に還元剤を供給することにより還元剤の前記低温酸化反応を生じさせ継続的に前記反応活性物質を生成し前記排気浄化触媒に空気過剰率が1.0以上の燃焼排気を供給し、前記排気浄化触媒上で生成した前記反応活性物質と排気中の NO_x とを反応させて排気中の NO_x を還元浄化する排気浄化方法が提供される。

【0009】すなわち、請求項1の発明では還元剤の低温酸化反応により反応活性物質を継続的に生成し、この反応活性物質と排気中の NO_x とを反応させて NO_x を還元浄化する。ここでいう反応活性物質とは、例えば炭化水素等のラジカル（遊離基）のことである。通常、酸化力の強い（活性化した）酸化触媒等で酸素過剰雰囲気下で炭化水素（HC）が酸化する場合にも酸化過程で中間生成物としてHCラジカルが発生するが、発生したラジカルは直ちに酸素と反応して CO_2 等に変化する。すなわち、酸化力の強い酸化触媒上でHCが酸化すると炭化水素の燃焼が生じる。

【0010】酸化触媒の活性が低い低温領域で還元剤を酸化させると、還元剤の酸化により生成したラジカルは直には酸素とは反応せずラジカル状態が維持される。また、この場合、触媒の活性が高い場合に比べて還元剤の酸化速度は遅く、供給された還元剤は一挙には酸化せず、比較的少量ずつ酸化していくため、触媒上では継続的にラジカルが発生するようになる。本明細書では、触媒の低温領域での上述の燃焼を伴わない酸化反応（継続的にラジカル成分が生成される酸化反応）を低温酸化反応と呼んでいる。また、低温酸化反応は、還元剤の酸化反応により発生する反応熱が還元剤の有する固有の発熱量より低くなる酸化反応とも言うことができる。炭化水素等のラジカルは、反応活性が非常に強く酸素の存在下においても NO_x 等の化学的に不安定な物質と優先的に反応する。

【0011】請求項1の発明では、酸化触媒を例えば活性化温度より低い比較的低温の領域で使用し、酸素過剰雰囲気下で（リーン空燃比の排気を触媒に供給しながら）炭化水素等の還元剤を触媒に供給する。これにより、触媒上では継続的に炭化水素等のラジカルが生成されるようになり、生成したラジカルは排気中の NO_x と反応し NO_x が還元浄化される。すなわち、低温酸化反

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応により生じた還元剤のラジカルを用いて NO_x を還元することにより、酸素過剰雰囲気を維持したままで高い効率で排気中の NO_x を還元浄化することが可能となる。

【0012】なお、気体状の還元剤を触媒に供給すると、低温酸化反応によるラジカルの生成速度が過大になり、過剰に生成したラジカルが酸素と反応して消費されるとともに、反応により触媒温度が上昇してしまい低温酸化反応が生じにくくなるおそれがある。このため、触媒に供給する還元剤は液体状のものを使用して、触媒上での蒸発の過程を経て低温酸化反応が生じるようにすることにより、比較的低い速度で継続的にラジカルが生成されるようにすることが好ましい。

【0013】請求項2に記載の発明によれば、前記排気浄化触媒に供給する燃焼排気の空気過剰率を1.0以上かつ1.7以下とする請求項1に記載の排気浄化方法が提供される。すなわち、請求項2に記載の発明では排気浄化触媒の雰囲気酸素濃度が低温酸化反応でラジカルが最も継続的に生成し易い条件に制御される。還元剤の低温酸化反応によりラジカルを生成するためには酸素が必要となる。このため、排気浄化触媒に供給する排気の空気過剰率は1.0以上である必要がある。一方、排気中の酸素濃度が高くなるにつれてラジカルの生成速度は速くなるが、この場合には供給した還元剤が短時間でラジカルに変化してしまい、触媒上に継続的にラジカルが存在する状態を実現することが困難になる場合がある。実験の結果、触媒上に継続して還元剤のラジカルが存在する状態を実現するためには空気過剰率が1.0以上かつ1.7以下の範囲が好ましいことが判明している。本発明では、排気浄化触媒に供給する排気の空気過剰率を1.0以上1.7以下とすることにより供給した還元剤により触媒上に継続的にラジカルを生成させ、排気中の NO_x を連続的に還元浄化可能としている。

【0014】請求項3に記載の発明によれば、前記排気浄化触媒は、酸化触媒成分と還元触媒成分とをそれぞれ酸化触媒成分による酸化能力と還元触媒成分による還元能力とがほぼ同等になる量だけ含む請求項1または請求項2に記載の排気浄化方法が提供される。すなわち、請求項3に記載の発明では、排気浄化触媒は酸化触媒成分に加えて還元触媒成分を含んでおり、還元触媒成分の還元能力が酸化触媒成分の酸化能力にほぼ拮抗するようにされている。前述したように、触媒の酸化能力が高いと供給された還元剤は一挙に燃焼してしまい低温酸化反応が生じなくなる。また、酸化触媒成分は一般的に温度が高くなるにつれて酸化能力が増大する。このため、酸化触媒成分のみを使用する場合には触媒が活性化する温度よりかなり低い温度で触媒に還元剤を供給する必要が生じ、触媒の使用温度範囲が狭くなる傾向がある。本発明では、排気浄化触媒に酸化触媒成分に加えて還元触媒成分を担持させることにより、相対的に酸化触媒成分の酸

化能力を低減するようにしている。これにより、触媒の温度が高くなっても排気浄化触媒全体としての酸化能力は増大せず、比較的高温でも還元剤の低温酸化反応を生じさせることが可能となる。すなわち、本発明では、酸化触媒成分に加えて還元触媒成分を排気浄化に担持させたことにより、広い温度範囲で還元剤ラジカルを触媒上に継続的に生成することが可能となっている。

【0015】請求項4に記載の発明によれば、前記排気浄化触媒は供給された還元剤を触媒内に保持し、酸素存在下の前記所定温度領域において、前記保持した還元剤の低温酸化反応を生じさせることにより触媒上に継続的に前記反応活性物質を生成する請求項1から請求項3のいずれか1項に記載の排気浄化方法が提供される。すなわち、請求項4に記載の発明では排気浄化触媒は供給された還元剤を触媒内に保持する機能を付与されている。この機能は、例えば触媒担体として水素吸蔵合金やペロブスカイト構造を有する物質等のように、構造内に炭化水素や水素等を吸着または吸収可能なものを使用することにより付与できる。触媒内に還元剤を保持可能とすることにより、保持された還元剤が所定温度領域において徐々に放出され触媒上で低温酸化反応を起こすようになる。このため、触媒上では還元剤のラジカルが継続的に発生するようになる。

【0016】請求項5に記載の発明によれば、内燃機関の排気通路に、供給された還元剤を保持し所定の活性化温度以上の触媒温度において酸素過剰雰囲気下で還元成分と排気中の NO_x とを選択的に反応させることが可能な、酸化触媒成分を含む排気浄化触媒を配置し、該排気浄化触媒に還元剤を供給し酸素過剰雰囲気下で前記排気浄化触媒温度を前記還元成分の沸点より高く、かつ前記活性化温度より低い所定の温度領域にすることにより、前記還元成分に燃焼を伴わずに酸化して反応活性物質を生成する低温酸化反応を生じさせ、生成した反応活性物質と機関排気中の NO_x とを反応させ排気中の NO_x を還元浄化する内燃機関の排気浄化方法が提供される。

【0017】すなわち、請求項5に記載の発明では、酸化触媒成分を含む排気浄化触媒を還元剤の低温酸化反応が生じる領域で使用することにより還元剤のラジカルを生成し排気中の NO_x を還元浄化する。前述したように、選択還元触媒等の排気浄化触媒は触媒温度が活性化温度以上である場合には、酸素過剰雰囲気下においても炭化水素等の還元剤と排気中の NO_x とを選択的に反応させて NO_x を還元することができるが、酸素過剰雰囲気下では還元剤と排気中の酸素との反応が支配的になるため NO_x の浄化率は低くなる。本発明では、酸化触媒成分を含む排気浄化触媒を所定の温度に維持することにより還元剤に低温酸化反応を生じさせるようにして酸素過剰雰囲気下においても NO_x の高い浄化率を達成する。還元剤の低温酸化反応により継続的に触媒上に還元剤の反応活性物質（ラジカル）を発生させることによ

り、過剰酸素雰囲気下においてもラジカルと NO_x との反応が優先的に起こるようになり排気中の NO_x が浄化される。なお、排気浄化触媒が活性化する温度では酸化触媒成分の能力が高くなっており還元剤の燃焼が生じるため、上記所定温度は活性化温度より低い温度とされる。また、排気浄化触媒に供給された還元剤が液状のままでは低温酸化反応は生じにくくなるため、上記所定温度は還元剤の沸点より高い温度であることが必要となる。

【0018】請求項6に記載の発明によれば、前記内燃機関の始動前に前記排気浄化触媒に前記還元剤を供給する請求項5に記載の内燃機関の排気浄化方法が提供される。すなわち、請求項6に記載の発明では内燃機関の始動前、すなわち排気浄化触媒に排気が到達する前に排気浄化触媒に還元剤を供給しておく。供給された還元剤は排気浄化触媒に吸着され、或いは排気浄化触媒表面上を覆った状態になる。

【0019】この状態で機関が始動して排気が排気浄化触媒に到達すると排気浄化触媒温度が上昇する。排気浄化触媒の温度が低温酸化反応が生じる領域に入ると供給された還元剤は排気浄化触媒上で気化し低温酸化反応を生じる。還元剤は機関始動前に触媒全体に供給されているため、この場合低温酸化反応は触媒全体で生じ触媒表面全体が生成したラジカルに覆われた状態になる。

【0020】機関を始動後 NO_x を含む排気が排気浄化触媒に供給されてから還元剤を供給すると生成したラジカルは直ちに NO_x と反応し消費される。このため、ラジカル生成速度と NO_x 流入量とのバランスがとれている間は、 NO_x がラジカルにより良好に浄化されるが、低温酸化反応によるラジカル生成速度は比較的に遅いため、一旦ラジカル生成と NO_x の流入とのバランスが崩れると例えば触媒が生成するラジカルの量が不足し排気中の NO_x が未反応のまま触媒を通過してしまう場合がある。また、触媒表面に NO_x や酸素が吸着された状態では還元剤のラジカルは生成しにくくなり、十分なラジカルが生成されない場合が生じる。本発明では、排気が到達する前に排気浄化触媒に還元剤を供給するため、排気浄化触媒の温度上昇時には機関停止中に触媒表面に吸着された酸素は還元剤と反応して消費される。このため、本発明では触媒全体で還元剤の低温酸化反応が生じようになり、触媒表面全体が生成されたラジカルで覆われるようになる。このため、排気中の NO_x が触媒表面に吸着されることが防止されるとともに、流入する NO_x 量の変動が生じてもラジカルが不足する事態が生じない。

【0021】請求項7に記載の発明によれば、前記排気浄化触媒は白金またはパラジウムを触媒成分として担持し、生成した前記反応活性物質を触媒成分表面に吸着可能である請求項5または請求項6に記載の内燃機関の排気浄化方法が提供される。すなわち、請求項7に記載の

発明では排気浄化触媒は白金またはパラジウムを触媒成分として担持している。白金やパラジウムは酸化触媒として機能し生成されたラジカルを表面上に良好に吸着する。これにより、低温酸化反応により生成されたラジカルは触媒表面を覆うようになる。

【0022】請求項8に記載の発明によれば、還元剤の供給を継続して行うことにより前記低温酸化反応により前記反応活性物質を触媒上に継続的に生成し、消費された反応活性物質を触媒に補充する請求項5から請求項7のいずれか1項に記載の内燃機関の排気浄化方法が提供される。すなわち、請求項8に記載の発明では還元剤の供給が継続的に行われる。このため、 NO_x との反応により消費されたラジカルが補充され触媒上には常に十分な量のラジカルが存在するようになり、ラジカルの不足による NO_x 浄化率の低下が生じない。なお、還元剤の継続的な供給とは、例えば常時少量の還元剤を触媒に連続的に供給する連続供給と、必要量の還元剤をある時間毎に供給する間欠供給との両方を含んでいる。

【0023】請求項9に記載の発明によれば、前記還元剤として液状炭化水素を使用し、炭化水素の性状に応じて触媒への還元剤の供給量または触媒温度の少なくとも一方を変化させることにより触媒上で所望量の前記反応活性物質を生成させる請求項5に記載の内燃機関の排気浄化方法が提供される。すなわち、請求項9に記載の発明では還元剤として液状炭化水素、例えば燃料油等が使用される。また、液状炭化水素はその性状により同一条件であっても炭化水素ラジカルの生成量が異なることが判明している。例えばセタン価の高い燃料油では同一条件でもセタン価の低い燃料油よりラジカルの生成量が大きい。

【0024】本発明では、供給する還元剤の性状により還元剤供給量と触媒温度の少なくとも一方を変化させることにより触媒上でのラジカルの生成量を制御する。例えばセタン価の低い燃料油を還元剤として使用する場合には、セタン価の高い燃料油を使用する場合に較べて燃料油供給量を増大するようにすれば生成するラジカルの量が低下することが防止される。また、ラジカル生成量は同一の燃料油であっても触媒温度の上昇とともに増大するため、セタン価の低い燃料油を使用する場合にはセタン価の高い燃料油を使用する場合に較べて触媒温度を上昇させるようにしても良い。

【0025】請求項10に記載の発明によれば、前記排気浄化触媒を通過後の排気中の特定成分濃度を検出し、該特定成分の濃度に応じて前記排気浄化触媒への還元剤供給条件を変化させる請求項5に記載の内燃機関の排気浄化方法が提供される。すなわち、請求項10に記載の発明では、排気浄化触媒通過後の排気中の特定成分濃度に応じて排気浄化触媒への還元剤供給条件を変化させる。ここで、排気中の特定成分としては、排気浄化触媒で生成される還元剤ラジカル（例えばアルデヒド基）や

NO_x成分等のように排気浄化触媒でのNO_xの浄化状態を表すものが使用される。例えば排気浄化触媒通過後の排気のNO_x濃度が高い場合（或いはラジカル成分濃度が低い場合）には、排気浄化触媒出でのラジカル生成量が少ないために未浄化のNO_xが下流側に流出したと考えられる。この場合には、排気浄化触媒への還元剤供給量を増大すること等により、排気浄化触媒上でのラジカル生成量を増大すれば未浄化のNO_xが下流側に流出することを防止できる。これにより、機関のNO_x生成量が変動するような場合にも常にNO_xの浄化効率を高く維持することが可能となる。

【0026】請求項11に記載の発明によれば、更に、前記排気浄化触媒の上流側に、酸化触媒成分を含み前記所定の温度領域において供給された還元剤に低温酸化反応を生じさせることの可能な上流側排気浄化触媒を配置し、該上流側排気浄化触媒の酸化能力を下流側の排気浄化触媒の酸化能力より小さくするようにした請求項5に記載の内燃機関の排気浄化方法が提供される。

【0027】すなわち、請求項11に記載の発明では、上流側に配置した酸化能力の比較的小さい排気浄化触媒と、下流側に配置した比較的大きな排気浄化触媒とを用いて低温酸化反応によりラジカルを生成する。前述したように、触媒上では還元剤の低温酸化反応が比較的低い速度で生じ還元剤のラジカルへの転換が一挙に生じることなくラジカルが継続的に生成されることがNO_xの浄化率を向上させるうえでは望ましく、このためには触媒の酸化能力は小さい方が好ましい。しかし、還元剤の低温酸化反応の速度が低いと、供給された還元剤のうちラジカルに転換されずそのまま触媒下流側に流出する量が増大することになる。本発明では、上流側に比較的大きな酸化能力の低い排気浄化触媒を配置し、この排気浄化触媒により還元剤に低温酸化反応を生じさせることにより継続的にラジカルを生成し排気中のNO_xを高い浄化率で浄化する。一方、この場合には還元剤の一部が排気浄化触媒上でラジカルに転換されることなく下流側に流出することになる。しかし本発明では、排気浄化触媒の下流側には酸化能力が比較的大きな排気浄化触媒が配置されているため、上流側の触媒を通過した未反応の還元剤は下流側の排気浄化触媒の一部が吸着され、残りは排気浄化触媒上で低温酸化反応によりラジカルに転換し、上流側の排気浄化触媒で浄化されなかった排気中のNO_xと反応する。このため、上流側の排気浄化触媒から流出する還元剤の大気への放出が防止されるとともに、全体としてのNO_xの浄化効率が更に向上する。

【0028】

【発明の実施の形態】以下、本発明の実施形態について説明する。以下の実施形態では、供給された還元剤（燃料油）を炭化水素ラジカルに転換することにより排気中のNO_xを浄化する排気浄化触媒が使用される。この触媒は、担持成分、構成等については公知の排気浄化触媒

と類似するが、従来の触媒とは全く異なる条件下で機能し排気中のNO_xを高効率で浄化する。このため、以下の説明では、従来の排気浄化触媒と区別するために本発明で使用される排気浄化触媒を便宜的にRAP（Radical Active Process）触媒と呼ぶことにする。

【0029】まず、最初にRAP触媒のNO_x浄化作用について説明する。RAP触媒は、白金（Pt）、パラジウム（Pd）等の酸化触媒成分を含む触媒であり、例えばPt、Pdを担持した選択還元触媒、或いはNO_x吸蔵還元触媒等もRAP触媒として使用することが可能である。これらの触媒は通常の使用法では、担持した酸化触媒成分の酸化能力が高くなる活性化温度（例えば300℃）以上の領域で使用される。活性化温度以上の触媒温度でこれらの酸化触媒成分に還元剤（燃料油）が供給されると、還元剤は触媒上で燃焼し、H₂O、CO₂に転換される。これに対して、RAP触媒では酸化触媒成分の活性化温度より低い温度範囲で還元剤（燃料油）を供給し、低温酸化反応を生じさせることによって炭化水素の中間酸化物を生成しこの中間酸化物から炭化水素のラジカル（遊離基）（例えばアルデヒド系ラジカル、カルボン酸系ラジカル、アルコール系ラジカル等）を生成する。これらのラジカルは反応活性が高くNO_x等の化学的に不安定な物質と特に反応し易いため、酸素過剰雰囲気下においても酸素との反応よりNO_xとの反応が優先されるようになる。

【0030】すなわち、RAP触媒に酸素過剰雰囲気下で炭化水素R・H（Rはアルデヒド基、メチル基等）が供給されると炭化水素が酸化されて、

$$R \cdot H + O_2 \rightarrow RO + OH$$

の反応により中間酸化物ROが生成される。この中間酸化物は更に触媒（Pt等）上で、 $RO \rightarrow R \cdot$ の反応によりR・（ラジカル）に転換される。

【0031】上記により生成したラジカルR・はNO_x（NO、NO₂等）と優先的に反応して、NO_xから酸素を奪い酸化物RO₂を生成する。すなわち、

$$R \cdot + NO_2 \rightarrow RO_2 + N_2$$

これにより、NO₂がN₂に還元される。触媒の活性化温度以上の領域における炭化水素の酸化反応においても中間酸化物ROは生成されているが、この領域では触媒の酸化能力が高いため生成された中間酸化物は酸素の存在下で直ちに酸化され最終酸化物RO₂になってしまうため、触媒の高温領域における酸化反応（燃焼）ではラジカルR・は生成されない。

【0032】上記の炭化水素ラジカルR・を生成する反応を本明細書では低温酸化反応と称しているが、低温酸化反応は、炭化水素の燃焼を伴わない酸化反応、或いは反応により生成される熱量が供給された炭化水素の発熱量より小さくなる領域での酸化反応として定義することができる。低温酸化反応には上述したように中間酸化物の生成のために酸素が必要となる。また、生成したラジ

カルは酸素存在下においても活発に NO_x と反応して NO_x を還元するため、高い NO_x 浄化率を達成することができる。このため、RAP触媒を空気過剰率が1.0より大きい燃焼排気が流通する排気通路に配置し、還元剤をRAP触媒に供給して低温酸化反応を生じさせることにより、RAP触媒上で生成した炭化水素ラジカルを用いて排気中の NO_x を還元浄化することが可能となる。この場合、従来の選択還元触媒では酸素存在下で NO_x の還元反応を行うため低い NO_x 浄化率しか達成できなかったのに対し、炭化水素ラジカルは酸素存在下においても NO_x と優先的に反応するため高い NO_x 浄化率を達成することが可能となる。また、従来の NO_x 吸蔵還元触媒では吸収した NO_x を還元浄化するために触媒に多量の還元剤を供給して触媒に流入する排気の空気過剰率を1.0以下に低下させる必要があり、排気の空気過剰率の複雑な制御が必要になっていたのに対して、RAP触媒触媒では流入する排気の空気過剰率を1.0以上（すなわちリーン空燃比）に固定したままで排気中の NO_x の還元浄化が可能となる利点がある。

【0033】RAP触媒を使用して、排気中の NO_x を高い効率で浄化するためには、(1)触媒上で低温酸化反応が生じること、及び、(2)低温酸化反応により継続的にラジカルが生成されること、の2つの条件を満足することが必要となる。これらの条件を満足するためには、触媒の温度、排気の空気過剰率、還元剤供給条件等を特定の範囲に調整することが好ましい。以下、これらの条件について説明する。

【0034】(1)触媒温度条件

前述したように、触媒の酸化能力が高い状態では供給された還元剤（燃料油）は触媒上で燃焼してラジカルを生成することなく CO_2 等の最終酸化物になってしまう。このため、触媒温度は少なくとも触媒の活性化温度より低く触媒の酸化能力が比較的低下する温度領域になければならない。また、触媒温度が低過ぎると酸化反応そのものが生じなくなる。また、RAP触媒に供給された還元剤が液体の状態になっていると化学反応が生じにくい。ため、少なくとも低温酸化反応が生じる状態では還元剤は気化している必要があり、触媒温度は供給された還元剤の沸点より高くなっている必要がある。更に、低温酸化反応が生じる温度領域でもラジカル生成速度は触媒温度が高いほど大きくなるが、ラジカル生成速度が過大になると供給した還元剤が一挙にラジカルに転換されてしまう。供給した還元剤が一挙にラジカルに転換されてしまうと、触媒上では一時的に還元剤が不足してラジカルの生成が停止してしまう。一方、供給した還元剤が一挙にラジカルに転換されると一度に多量のラジカルが触媒上に生成されるが、このラジカルはそのまま触媒上に残留するわけではなく NO_x の還元で使用されなかった過剰なラジカルは排気中の酸素と反応して消費されてしまう。このため、ラジカル生成速度、すなわち低温酸化反

応の速度が大き過ぎると触媒上に一時的にラジカルが存在しない状態が生じ、 NO_x を浄化することができない。従って、触媒温度は低温酸化反応の速度が比較的低下する領域とする必要がある。

【0035】すなわち、上記から NO_x 浄化のためのRAP触媒触媒温度は、少なくとも酸化触媒成分の活性化温度より低く、しかも供給する還元剤の沸点より高いことが必要とされ、更に比較的低い反応速度で低温酸化反応が生じることが必要とされる。この温度領域は、使用する触媒成分や還元剤の種類によっても異なってくるが、例えば、軽油を還元剤として使用する場合には約170℃が下限温度となる。

【0036】また、上記温度領域の上限については、触媒の酸化能力が高いほど低くなる傾向があり、酸化能力が高い触媒を使用する場合には低くなり、酸化能力が低い触媒を使用する場合には高くなる。また、酸化能力の高い酸化触媒を担持させる場合にも、同時に還元触媒成分（例えばロジウム（Rh））を酸化触媒とともに担持させることにより上記温度領域の上限を高くすることが可能である。

【0037】すなわち、還元触媒成分を酸化触媒に加えて担持させることにより酸化触媒成分の酸化能力が還元触媒成分の還元能力により抑制されるため、触媒全体としての酸化能力は高温の領域でも比較的小さくなる。特に、酸化触媒成分による酸化能力と還元触媒成分による還元能力とがほぼ同等になるような量の酸化触媒成分と還元触媒成分とを触媒に担持させると低温酸化反応が生じる上限温度を大きく拡大することが可能となる。例えば、Pt、Pd等の酸化触媒成分のみを担持させた場合には活性温度（300℃）以上では低温酸化反応は生じないが、Pt、Pd等の酸化触媒とともに、ロジウム（Rh）等の還元触媒成分を担持させることにより低温酸化反応の上限温度は430℃程度まで上昇することが判明している。

【0038】従って、 NO_x 浄化のためのRAP触媒の使用温度領域は約170℃～約430℃程度となる。

(2)排気の空気過剰率

上述したように、低温酸化反応によるラジカル生成のためには酸素が必要となる。このため、RAP触媒は酸素過剰雰囲気調整する必要があり、触媒に供給する排気の空気過剰率は1.0以上となっている必要がある。

【0039】一方、低温酸化反応の反応速度は排気中の酸素濃度が高いほど高くなる。このため、排気中の酸素濃度が過度に高くなると反応速度の増大のために供給された還元剤が一挙にラジカルに転換されてしまい、触媒温度が高い場合と同様に継続的にラジカルを生成することができなくなる問題が生じる。このため、排気の空気過剰率は1.0以上の特定の範囲にあることが必要とされる。この空気過剰率の範囲は使用する触媒、温度条件等によっても変化するが、Pt、Pdを担持させたRA

P触媒では実験の結果空気過剰率が1.0～1.7の範囲にあるときに最も高いNO_x浄化効率を得られることが判明している。

【0040】通常、ディーゼル機関の場合には運転時の空気過剰率は1.6程度までは低下させることが可能であるため、上記空気過剰率はディーゼル機関でも十分に達成可能な範囲となっている。

(3) 還元剤供給条件

上述したように、NO_xを高効率で浄化するためには供給された還元剤が一挙にラジカル化しないで比較的低い反応速度で継続的に触媒上にラジカルを生成し続けることが望ましい。このためには、還元剤を液体の状態ではR A P触媒に到達させることが好ましい。還元剤が気体状態で触媒に到達すると触媒上では反応が急激に進んでしまい、供給された還元剤が一挙にラジカルに転換される場合が生じるからである。還元剤が液状のまま触媒に到達すると、還元剤が触媒上で気化する過程を経てから低温反応を生じるため、気化の過程で気体状の還元剤が比較的緩やかな速度で還元剤に供給されるようになる。このため、液体状の還元剤を供給することにより、ラジカル生成速度が低くなり触媒状態で継続的にラジカルが生成するようになる。

【0041】上記のように、R A P触媒で排気中のNO_xを高効率で浄化するための条件は以下になる。

(1) 触媒温度を、供給する還元剤の沸点以上であり、担持した酸化触媒成分の活性化温度より低い特定の低温反応が生じる温度（例えば170℃～430℃）に維持する。

【0042】(2) 排気の空気過剰率を1.0以上の、ラジカル生成速度が過大にならない範囲（例えば1.0～1.7程度）に維持する。

(3) 液体の還元剤を使用し、還元剤が液体状態のまま触媒に到達するようにする。

以下に説明する実施形態では、R A P触媒を使用して上記(1)から(3)の条件を満たすことによりNO_xの高い浄化効率を達成している。

【0043】①第1の実施形態

図1は、本発明の排気浄化方法の第1の実施形態を実施する排気浄化装置の概略構成を説明する図である。図1において、3は内燃機関、火炉等の燃焼排気流れる排気通路、10は排気通路3に配置された後述するR A P触媒を示す。本実施形態では、触媒10の上流側の排気通路に液体還元剤を供給する還元剤供給装置20が設けられている。

【0044】還元剤供給装置は、ポンプ、加圧タンク等の加圧還元剤供給源21と、供給源21から供給される還元剤を触媒10上流側の排気通路3内に噴射する還元剤ノズル23とを備えている。図1に25で示すのは、加圧供給源21からノズル23に供給される還元剤の流量を調節する制御弁である。本実施形態で使用される還

元剤としては、触媒10上で気化して炭化水素を生成する液体炭化水素が使用され、例えば比較的気化しにくい灯油、軽油等の燃料油が使用される。還元剤ノズル23は、噴射された燃料油が排気中で気化することなく液状のまま触媒10に到達するように触媒10に近接した位置に配置されている。

【0045】本実施形態で使用するR A P触媒は、例えば、白金(Pt)、パラジウム(Pd)等の酸化触媒成分を多孔質ゼオライト（例えばZ S M 5等）に担持したものとされ、一般的なPt/Pd系の選択還元触媒と同様な構成とされている。また、排気通路3に流通する燃焼排気は空気過剰率が1.0～1.7の範囲になるように内燃機関や火炉の燃焼状態が調整されている。また、触媒10入口での排気温度は供給される還元剤の沸点（例えば170℃）より高く、触媒10の酸化触媒成分の活性化温度（例えば300℃程度）より低い、触媒10上で還元剤の低温酸化反応が生じる温度範囲になるように触媒10と内燃機関または火炉等の排気発生源との距離が設定されている。

【0046】本実施形態では、マイクロコンピュータ等の制御装置30により制御弁25の開度を調節することにより、ノズル23から噴射する還元剤の流量を制御している。ノズル23からの還元剤噴射量は、排気通路3を流れる排気流量及びNO_x濃度に応じて制御される。ノズル23から噴射された還元剤は液状のまま触媒10に到達し、触媒10上で比較的緩やかに蒸発する。上述したように、本実施形態では排気温度、空気過剰率が触媒上で低温酸化反応が生じる範囲に調節されているため、触媒上では気化した還元剤が中間酸化物R Oを経てラジカルに転換され、生成したラジカルが排気中のNO_xと優先的に反応することにより排気中のNO_xが高効率で浄化される。

【0047】なお、ノズル23からの還元剤の噴射は、連続的に行っても良いし、パルス状に間欠的な噴射を行っても良い。本実施形態では、炭化水素を吸着可能な触媒担体が使用されているため、間欠的に還元剤を噴射した場合も供給された還元剤の一部は触媒10の担体に吸着され、その後担体から浸出して低温酸化反応を生じるため、触媒10上ではラジカルが継続して生成され続けるようになる。

【0048】また、本実施形態ではPt、Pd等の酸化触媒のみを触媒10上に担持しているが、これらの酸化触媒に加えてロジウムRh等の還元触媒成分を触媒10上に担持させ、全体としてPt、Pd等の成分の酸化能力とRh等の成分の還元能力とが略同等となるようにすれば、更に高温の領域でも高いNO_x浄化効率を維持することが可能となる。

【0049】②第2の実施形態

図2は本発明の排気浄化方法の第2の実施形態を実施する排気浄化装置の概略構成を説明する図である。本実施

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形態では、第1の実施形態と同様なRAP触媒10を内燃機関（本実施形態ではディーゼル機関）1の排気通路3に配置している。

【0050】図2に20で示すのは第1の実施形態と同様な還元剤ノズル23、制御弁25及び還元剤供給源21を備えた還元剤供給装置である。本実施形態では、還元剤としては機関1の燃料と同じディーゼル燃料油が使用される。更に、本実施形態では、還元剤ノズル23の上流側に空気を噴射する搬送空気供給装置40が設けられている。搬送空気供給装置40は還元剤ノズル23の上流側の排気通路3に配置されたエアノズル41と、ノズル41に機関始動前に加圧空気を供給可能な電動エアポンプ、エアタンク等の加圧空気供給源43を備えている。

【0051】本実施形態では、機関1始動前（例えばメインスイッチがオンにされてから機関始動操作が行われるまでの間）に触媒10に還元剤を供給する。すなわち、制御装置30は機関1のエンジンキーが挿入されたことを検知すると、電動エアポンプ43を起動してエアノズル41から排気通路3中にエアを供給する。このエアにより排気通路3には、触媒10を通して流れる空気流が生じる。また、同時に制御回路30は制御弁25を開弁して還元剤ノズル23から燃料油を噴射する。これにより、還元剤ノズル23から噴射された燃料油はエアノズル41から噴射されたエアにより生じる搬送空気流に乗って触媒10に到達し、触媒10の表面に付着する。制御回路30は、予め定めた時間だけエアノズル41からのエア噴射と還元剤ノズル23からの燃料油噴射とを行った後で機関1を始動する。ここで、燃料油噴射を行う時間は、ノズル23から噴射された燃料油により触媒10表面全体が覆われるのに必要な時間とされ、実験等により定められる。

【0052】これにより、触媒10表面全体が還元剤で覆われた状態で機関1が始動される。本実施形態では、ディーゼル機関1は通常よりも低い空気過剰率（例えば空気過剰率で1.6程度）で運転されるように機関1の燃料噴射量が設定されている。また、触媒10は、通常運転時に触媒10に到達する排気温度が前述した低温酸化反応が生じる温度範囲の上限を越えない位置に配置されている。

【0053】機関1が始動して機関の排気が触媒10に到達するようになると、触媒10の温度は上昇し、前述した還元剤の低温酸化反応が生じる温度領域になる。この時、触媒10の全表面を覆った還元剤（燃料油）が気化を開始する。また、機関1の排気の空気過剰率は1.6程度になっているため、触媒10の温度が低温酸化反応が生じる温度領域になると、触媒10の全体で燃料油が低温酸化反応を生じ徐々にラジカルを生成するようになり、触媒10全体でPt、Pd等の触媒成分表面に生成したラジカルが吸着され触媒成分表面がラジカルで覆

われるようになる。このラジカルは排気中のNO_xと反応しNO_xを浄化しながら消費されていく。このため、機関始動後に触媒10への還元剤の供給を停止したままでは、始動前に供給された還元剤はやがて消費されてしまい、触媒10表面上にラジカルが吸着されていない状態が生じる。触媒10表面にラジカルが存在しない状態では、排気中の酸素やNO_xがPt、Pd等の触媒成分表面に吸着されてしまい、この部分では還元剤を供給してもラジカルが生成されにくくなる。

【0054】このため、本実施形態では機関が始動した後は還元剤ノズル23からの還元剤の供給を継続的にを行い、触媒10表面全体に常にラジカルが吸着された状態になるようにしている。機関始動後のノズル23からの還元剤の噴射量は触媒10でNO_xとの反応により消費されるラジカルを補充可能な量とされる。これにより、触媒10上ではNO_xとの反応に消費されるラジカルと略同等の量のラジカルを生成する還元剤が供給されるようになり、常に触媒表面全体がラジカルで覆われた状態が継続するようになる。

【0055】このように、触媒10表面全体にラジカルが吸着された状態を継続することにより、例えば機関運転条件の変化により排気中のNO_x濃度が多少増大した場合でも、ラジカルを十分に確保することができるため、運転条件の変動等によりラジカル不足が生じ未浄化のNO_xが流出することが防止される。なお、本実施形態においても還元剤ノズル23からの還元剤の噴射は連続的であっても良いし、パルス状に間欠的に行っても良い。

【0056】③第3の実施形態

本実施形態では、図2と同じ構成の装置を用いて機関1の運転中に還元剤の性状に応じて機関運転状態や還元剤供給量を変化させて触媒10上で常に所定量のラジカルが生成されるようにする。RAP触媒でのラジカル生成量（生成速度）は、温度条件や酸素濃度、還元剤の供給量等の条件が同一であっても還元剤の性状によって変化する。例えば還元剤としてディーゼル燃料油を供給する場合には燃料油のセタン価が高いほど同一条件でもラジカル生成量が大きいことが判明している。

【0057】このため、同一の条件で還元剤を供給していると機関1の燃料としてセタン価の低いものを使用した場合には触媒10上で生成するラジカル量が不足して未浄化のNO_xが触媒下流側に流出する場合がある。そこで、本実施形態では、機関1の燃焼室内圧力をモニターすることにより、使用燃料のセタン価を検出し、セタン価に応じて触媒温度や還元剤供給量等の反応条件を変更するようにしている。

【0058】まず、燃焼室内圧力による使用燃料のセタン価検出方法について説明する。図3はディーゼル機関の燃焼室の圧縮行程と爆発行程における圧力変化を模式的に示す図である。図3において圧縮行程ではピスト

ンの上昇により燃焼室内圧力は上昇し、圧縮行程上死点付近(図3、A点)で燃料が噴射されると、燃料の燃焼により上死点付近で燃焼室内圧力は急上昇する。図3に示すように燃料が噴射されるまでは圧縮行程における燃焼室内圧力は滑らかに上昇する。

【0059】ディーゼル機関では圧縮行程の早い時期は圧縮による温度上昇が少なく燃焼室内空気の温度が低く燃料の着火温度に到達していないため圧縮行程早期に燃料噴射を行っても燃焼室は生じず、本来は図3に実線で示すように滑らかに圧力が上昇するはずである。しかし、実際には圧縮行程早期(例えば、図3、B点)に少量の燃料を噴射すると図3に点線で示すように噴射後圧力が一時的に上昇する。しかし、この場合も燃焼は生じないため一時的に上昇した圧力は、その後通常の圧縮行程時の圧力変化(実線)に一致するようになる。

【0060】図3のように、圧縮行程早期に燃料噴射を行った場合に噴射後一時的に圧力が上昇する理由は、燃料油中に含まれるセタン価の低い直鎖状の炭化水素成分が酸化して中間酸化物ROが形成され、その際の反応熱により一時的な圧力上昇が生じるものと考えられる。また、燃料中にセタン価の低い炭化水素成分が多く含まれるほど、すなわち燃料油のセタン価が高いほど上記反応が活発となるため、通常の圧縮行程中の圧力と圧縮行程早期の燃料噴射後の圧力上昇のピークとの差(図3、 ΔP)は燃料油のセタン価が高い程大きくなる。このため、この圧力差 ΔP を燃料油のセタン価を表す指標として用いることができる。

【0061】本実施形態では、機関1の特定の気筒に燃焼室内圧力を検出可能な燃焼室圧センサを配置しており、機関の運転中定期的にセタン価測定のために気筒圧縮行程の早い時期に少量の燃料を噴射し、その後の圧力上昇のピーク値を検出する。そして、このピーク値と通常の圧縮行程における同時期の燃焼室内圧力との差 ΔP を算出し、使用燃料のセタン価を推定する。

【0062】また、本実施形態では制御回路30は、上記により推定されたセタン価に基づいて常に必要量のラジカルが触媒10上で生成されるように触媒10における反応条件を調節する。例えば、使用燃料のセタン価が低い場合には触媒上でのラジカルの生成量が低下する。このため、制御回路30は、還元剤ノズル23からの還元剤噴射量を増大することにより、触媒上でのラジカルの生成量の低下を防止する。これにより、使用する還元剤の性状の変化による NO_x 浄化率の低下が防止される。

【0063】なお、触媒10でのラジカルの生成速度は触媒温度が高いほど大きくなる。このため、使用燃料のセタン価が低い場合には機関の負荷条件を変化させて触媒に到達する排気温度を上昇させるようにしても良い。また、触媒10でのラジカル生成速度は、排気の酸素濃度が高いほど大きくなる。このため、使用燃料のセタン

価が低い場合には、機関への燃料噴射量を低減して排気の空気過剰率を上昇させるようにしても良い。

【0064】④第4の実施形態

前述したように、RAP触媒上でのラジカルの生成量は触媒温度と雰囲気酸素濃度に応じて変化する。ところが、内燃機関の排気通路にRAP触媒を配置した場合には、触媒温度と雰囲気酸素濃度は排気温度と排気の空気過剰率により定まることになるため、機関運転状態の変化等により排気温度や空気過剰率が変化するとそれに応じて触媒上でのラジカル生成量が変化してしまう。また、触媒上でのラジカルの生成量は排気中の NO_x 量に応じて調節する必要がある。

【0065】そこで、本実施形態ではラジカル生成量を支配する条件(例えば排気温度、空気過剰率)等の変化に応じて触媒への還元剤供給条件を変えることにより機関運転条件の変化によるラジカル生成量の変動を防止するとともに、排気中の NO_x 量に応じて触媒上でのラジカル生成量を制御するようにしている。図4は、本実施形態の排気浄化方法の第4の実施形態を実施する排気浄化装置の概略構成を示す図である。図4において、図3と同一の参照符号は図3のものと同様の要素を示している。

【0066】本実施形態では、排気通路3の還元剤ノズル23上流側には排気中の酸素濃度を計測可能な酸素濃度センサ31が配置されている。また、RAP触媒10下流側の排気通路には排気温度を検出する温度センサ33及び排気中の NO_x 濃度を検出する NO_x センサ35が配置されている。制御回路30は酸素濃度センサ31から入力する酸素濃度C、温度センサ33から入力する排気温度T及び NO_x センサ35から入力する NO_x 濃度C NO_x を一定時間毎に監視し、前回からの酸素濃度C、排気温度T、 NO_x 濃度C NO_x の変化量 ΔC 、 ΔT 、 $\Delta C\text{NO}_x$ を算出するとともに、これらの変化量に基づいて還元剤ノズル23からの還元剤の噴射量を制御する。

【0067】例えば、排気酸素濃度変化量 ΔC が正の場合には触媒10上でのラジカル生成量は増大傾向にあるため制御回路30は、 ΔC が正の値である限り還元剤ノズル23からの還元剤噴射量を一定量ずつ減少させる。また、反対に ΔC が負の値である場合には触媒10上でのラジカル生成量は減少傾向にあるため、制御回路30は ΔC が負の値である限り還元剤ノズル23からの還元剤噴射量を一定量ずつ増大させる。

【0068】また、同様に排気温度変化量 ΔT が正の値の場合には、ラジカル生成量は増大傾向にあり、 ΔT が負の値の場合にはラジカル生成量は減少傾向にある。このため、制御回路30は ΔT の値が正である限り還元剤噴射量を一定量ずつ減少させ、負の値である限り還元剤噴射量を一定量ずつ増大させる。また、 NO_x 濃度変化量 $\Delta C\text{NO}_x$ が正の値である場合には、機関排気中のN

O_x量が増加した等のために触媒10上でラジカルが不足したことを意味するため、できるだけ速く触媒10上でのラジカル生成量を増大させる必要がある。そこで、この場合には制御回路30は還元剤噴射量を ΔCNO_x に比例する量だけ増大するようにする。

【0069】このように、排気温度と排気酸素濃度、触媒10下流側の排気NO_x濃度に応じて還元剤噴射量を制御することにより、常に触媒10上に適量のラジカルを生成することが可能となり、ラジカルの不足により未浄化のNO_xが触媒下流側に流出することが防止される。なお、本実施形態では、触媒10下流側の排気NO_x濃度に応じて還元剤噴射量を調節する制御を行っているが、排気NO_x濃度に加えて、または排気NO_x濃度とともに触媒10下流側の排気中のラジカル成分濃度（例えばアルデヒド濃度）を検出し、ラジカル成分濃度に応じて還元剤噴射量を調節する制御を行っても良い。すなわち、触媒上でのラジカル量がNO_x量に対して不足する傾向にあると触媒下流側に流出するラジカル成分の量は減少する。このため、触媒10下流側排気のラジカル成分濃度が減少した場合には還元剤噴射量を増大する制御を行うことによっても触媒10上に常に適量のラジカルを生成することが可能となる。

【0070】第5の実施形態

図5は本発明の排気浄化方法の第5の実施形態を実施する排気浄化装置の概略構成を説明する図である。図5において、図2と同一の参照符号は同様な要素を示している。本実施形態においても、機関1の排気通路3上には図2と同様なRAP触媒からなる排気浄化触媒10が配置されている。しかし、本実施形態では排気浄化触媒10の上流側で還元剤ノズル23の下流側の排気通路3に別のRAP触媒（上流側排気浄化触媒）15が配置されている点が相違している。

【0071】本実施形態の上流側排気浄化触媒15は、排気浄化触媒10（下流側排気浄化触媒）と同様にPt、Pd等の酸化成分を担持しており下流側排気浄化触媒10と同様に還元剤の低温酸化反応を生じることが可能である。但し、本実施形態の上流側排気浄化触媒15はアルミナ等の担体を使用しており、供給された還元剤を吸着、保持する機能は有していない点が下流側排気浄化触媒10と相違している。また、上流側排気浄化触媒15のPt、Pd等の酸化成分の担持量は下流側排気浄化触媒15より少くされており、上流側排気浄化触媒15の酸化能力は下流側排気浄化触媒10の酸化能力より小さくなっている。

【0072】本実施形態においても、ディーゼル機関1は比較的低い空気過剰率（例えば1.6程度）で運転され、触媒10、15は機関運転中に触媒に到達する排気温度が触媒10、15において還元剤の低温酸化反応が生じる上限温度を越えない位置に配置されている。本実施形態においても機関運転中には還元剤供給装置20の

還元剤ノズル23から液体状の還元剤（ディーゼル燃料油）が噴射される。噴射された還元剤は、上流側排気浄化触媒15上で低温酸化反応を生じ、触媒上で生成したラジカルにより排気中のNO_xが還元浄化される。本実施形態では、上流側排気浄化触媒15の酸化能力は下流側排気浄化触媒10に較べて小さくなるように触媒成分量が設定されている。前述したように、触媒上で低温酸化反応により継続的にラジカルを生成するためには、触媒の酸化能力は小さい方が好ましい。このため、酸化能力の低い上流側排気浄化触媒15上では継続的にラジカルが生成され、NO_xの浄化率が高くなる。

【0073】ところが、本実施形態では上流側排気浄化触媒15の酸化能力を小さく設定したことによりNO_xの浄化率を向上させることができるものの、酸化能力が小さいため上流側排気浄化触媒15では供給された還元剤のうち酸化されずに触媒15を通過する還元剤の量が増大してしまう。上流側排気浄化触媒15として、下流側排気浄化触媒10と同様な炭化水素吸着能力を有するものを使用すればある程度この問題は防止されるものの、その場合にも多少の炭化水素が下流側に流出するため、排気性状の悪化が生じるおそれがある。

【0074】そこで、本実施形態では上流側排気浄化触媒15には炭化水素の吸着能力を付与せずに、未反応の炭化水素はその全量が下流側に流出するようにして、下流側に設けた排気浄化触媒10により排気の浄化を行う。すなわち、本実施形態では、比較的多量の炭化水素が上流側排気浄化触媒15で反応することなく下流側排気浄化触媒10に流入する。本実施形態では、下流側排気浄化触媒10においても低温酸化反応が生じる温度酸素条件が成立しているため、下流側排気浄化触媒10に到達した炭化水素は一部がラジカルに転換され、上流側排気浄化触媒15で浄化されなかった排気中のNO_xを還元する。また、炭化水素の残りの部分のうち一部は、酸化能力の大きい下流側排気浄化触媒10上で酸化され、酸化されない炭化水素は下流側排気浄化触媒10に吸着保持される。このため、本実施形態ではNO_xの浄化率を更に向上させるとともに未反応の炭化水素の大気放出をほぼ完全に防止することが可能となっている。

【0075】

【発明の効果】各請求項に記載の発明によれば、触媒に流入する排気空燃比をリッチ空燃比に調整する操作を行うことなく、高いNO_x浄化効率を達成することが可能となるという共通の効果を奏する。

【図面の簡単な説明】

【図1】本発明の排気浄化方法の第1の実施形態を実施する排気浄化装置の概略構成を示す図である。

【図2】本発明の排気浄化方法の第2の実施形態を実施する排気浄化装置の概略構成を示す図である。

【図3】本発明の排気浄化方法の第3の実施形態を説明する図である。

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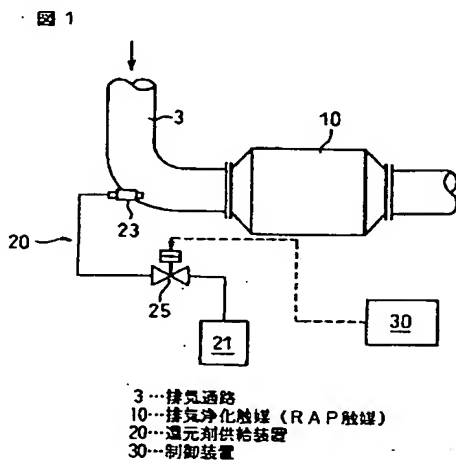
【図 4】本発明の排気浄化方法の第 4 の実施形態を実施する排気浄化装置の概略構成を示す図である。

【図 5】本発明の排気浄化方法の第 5 の実施形態を実施する排気浄化装置の概略構成を示す図である。

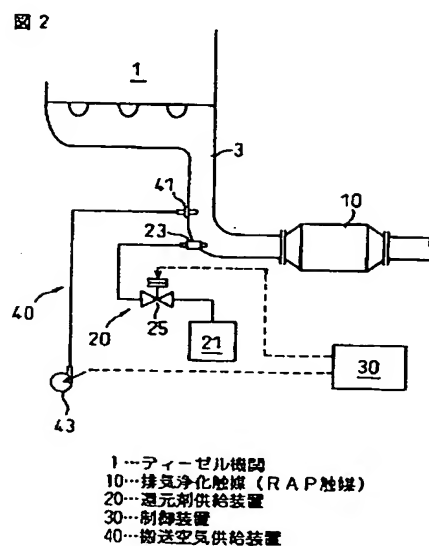
【符号の説明】

- * 1 … 内燃機関
 --- 3 … 排気通路
 10、15 … RAP 触媒
 20 … 還元剤供給装置
 * 30 … 制御装置

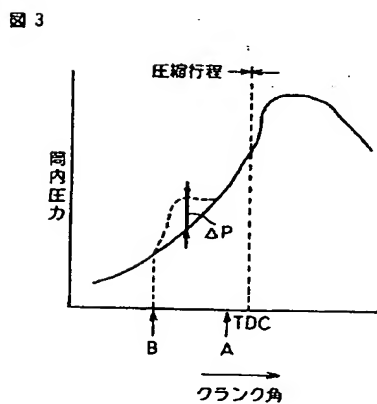
【図 1】



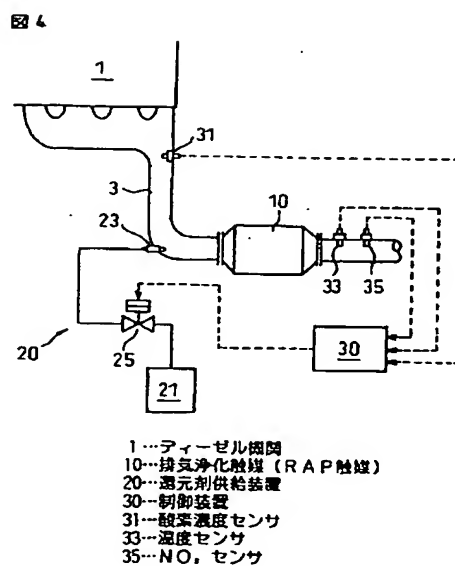
【図 2】



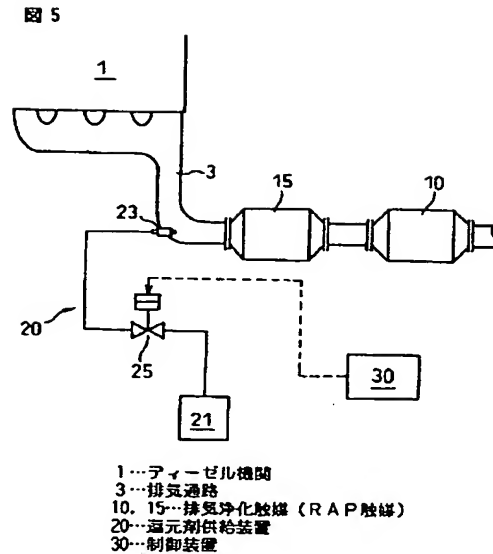
【図 3】



【図 4】



【図 5】



フロントページの続き

(51)Int.Cl.⁷

F 0 1 N 3/10
3/20
3/36

識別記号

F I

F 0 1 N 3/36
B 0 1 D 53/36

テーマコード (参考)

B
Z A B
1 0 1 B

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F ターム (参考) 3G091 AA18 AA28 AB02 AB05 BA01
BA03 BA04 BA14 BA39 CA18
CA22 CB02 CB03 CB08 DA01
DA02 DB10 EA12 EA17 EA26
EA33 EA34 FA02 FA04 FA12
FA13 FB02 FB10 FC04 FC07
GA06 GA18 GA19 GB05W
GB06W GB07W GB09X HA08
HA37 HB07
4D048 AA06 AA19 AB01 AB02 AB06
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